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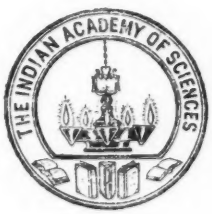

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PRODUCTION OF BURSTS AND THE SPIN OF THE MESON

By H. J. Bhabha, H. Carmichael
and
C. N. Chou

Received October 5, 1939
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

It was shown some time ago (Bhabha, 1938) that mesons, which form the main body of the penetrating component of cosmic radiation, may produce showers at least by the following process. A meson occasionally makes a very close collision with an atomic electron, communicating a large energy to it. This electron then produces a shower by the ordinary cascade process. The original calculations were however based on the assumption that the meson is described by the Dirac equation, thus attributing a spin of half a unit to it like the electron. Since it is now believed that the meson is responsible for nuclear interactions, the dependence of nuclear forces on the orientations of the spin of nuclear particles makes it necessary for the meson to have a spin of one unit. In this case it would have to be described by the equations given by Proca (1936).

Massey and Corben (1939) have recently considered the collision of a meson with an electron on the quantised theory[1] of a meson with a spin of one unit. They find that the differential cross-section for the collision of a meson of energy $\gamma \mu c^2$, μ being the meson mass, with a free electron at rest, in which the electron acquires a fraction q of the original energy of the meson is given by

$$Q^{(1)}(q)\,dq = 2\pi\left(\frac{e^2}{mc^2}\right)^2 \frac{\theta\gamma}{\gamma^2-1}\left[1-\frac{\gamma^2-1}{\gamma^2}\frac{q}{q_m}+\frac{q\theta}{\gamma^2}(2\gamma^2+1)\right.$$
$$\left.+\frac{q^2}{6}(1-2\theta\gamma-\theta^2)+\frac{q^3\theta\gamma}{6}\right]\frac{dq}{q^2}. \qquad (1)$$

Here q_m is the maximum value of q and is given by

$$q_m = \frac{2\theta(\gamma^2-1)}{\gamma(1+\theta^2+2\theta\gamma)}. \qquad (2)$$

The cross-section for the same process calculated by Bhabha (1938) assuming that the meson obeys the Dirac equation is

$$Q^{(\frac{1}{2})}(q)\,dq = 2\pi\left(\frac{e^2}{mc^2}\right)^2 \frac{\theta\gamma}{\gamma^2-1}\left[1-\frac{\gamma^2-1}{\gamma^2}\frac{q}{q_m}+\tfrac{1}{2}\frac{\gamma^2}{\gamma^2-1}q^2\right]\frac{dq}{q^2}. \qquad (3)$$

For small q the two cross-sections are practically the same, so that the ionisation loss is not affected, but for large γ and $q \sim 1$ the two cross-sections

[1] Kemmer (1938), Fröhlich, Heitler and Kemmer (1938), Bhabha (1938 *a*), Yukawa, Sakata and Taketani (1938), Stueckelberg (1938).

are very different. There are terms proportional to γ in the square brackets in (1), whereas similar terms are absent in (3). Large knock-on showers can only be produced by very fast mesons with very large values of γ. We should therefore expect (1) to lead to markedly more large knock-on showers than (3) although the total soft component accompanying the penetrating particles would not be greatly altered since large showers are very rare.

Using the cross-section (1) and the general method of the previous paper (Bhabha, 1938) we have calculated the probability of a meson of given energy emerging accompanied by a shower of *more than* N particles from an " infinitely thick" layer of a substance. In order to compare our results with experiment, we have then integrated this probability over the spectrum of the mesons at sea-level and in a tube station. Following Euler and Heisenberg (1938) we have assumed that the number of mesons of energy above E at a depth T below the top of the atmosphere is given to a good approximation by

$$F(T, E) = I_0 \left(\frac{2.\ 10^9 \text{ e.v.}}{\epsilon T + E} \right)^{\delta} \qquad (4)$$

for the high energies concerned, where $\delta = 1 \cdot 87$, and

$$\epsilon T = \begin{cases} 2 \cdot 10^9 \text{ e.v. at sea-level} \\ 12 \cdot 10^9 \text{ e.v. in the tube station.} \end{cases}$$

Our results are given in Table I. It clearly shows that whereas the frequency of the smaller showers is approximately the same on the two theories, for the larger showers the new theory gives probabilities which are many times greater than the old one.

TABLE I

	Spin / N	Air		Lead	
		½	1	½	1
Sea-Level	10	$1 \cdot 29 \times 10^{-1}$	$1 \cdot 61 \times 10^{-1}$	$3 \cdot 17$	$2 \cdot 96$
	100	$5 \cdot 14 \times 10^{-4}$	$2 \cdot 87 \times 10^{-3}$	$5 \cdot 2 \times 10^{-2}$	$7 \cdot 6 \times 10^{-2}$
	1000	$8 \cdot 0 \times 10^{-7}$	$6 \cdot 4 \times 10^{-5}$	$2 \cdot 26 \times 10^{-4}$	$1 \cdot 15 \times 10^{-3}$
Tube Station	10	$7 \cdot 87 \times 10^{-2}$	$1 \cdot 10 \times 10^{-1}$	$7 \cdot 6 \times 10^{-1}$	$7 \cdot 6 \times 10^{-1}$
	100	$4 \cdot 88 \times 10^{-4}$	$2 \cdot 74 \times 10^{-3}$	$3 \cdot 03 \times 10^{-2}$	$4 \cdot 11 \times 10^{-2}$
	1000	$8 \cdot 0 \times 10^{-7}$	$6 \cdot 4 \times 10^{-5}$	$2 \cdot 13 \times 10^{-4}$	$1 \cdot 09 \times 10^{-3}$

The columns headed ½ give the old results obtained by using (3) whereas the columns headed 1 give the new results obtained by using (1).

Plotting the frequency of bursts containing more than N particles as a function of N on a log log scale, both theories give practically straight lines, but the new theory gives a much smaller slope than the old theory. Comparison of the theoretical curves with recent experiments by two of us (H. C. and C. N. C.) in which frequency size curves of bursts produced in "air" and lead have been obtained both at sea-level and in a tube station, definitely shows that the new theory agrees much better with experiment than the old theory. Recent experiments by Lovell[2] (1939) on knock-on showers of 5–50 particles also seem to show that the old theory gives fewer large showers than are observed.

A detailed analysis of experimental conditions has shown that it is not possible to conclude, as has been done hitherto, that the relative frequencies of showers in light and heavy elements are in disagreement with theory. Thus the frequency-size curve of bursts provides evidence that the meson has a spin of one unit in agreement with what is believed from nuclear considerations. This work was carried out in Cambridge in June, but external circumstances followed by the outbreak of war have delayed its publication. This short note is therefore being published now. The detailed calculations and a discussion of the comparison with experiment will be published elsewhere.

REFERENCES

Bhabha	..	*Proc. Roy. Soc.*, (A), 1938, **164**, 257–94.
———	..	*Ibid.*, 1938 *a*, **166**, 501–28.
Euler and Heisenberg	..	*Ergebnisse der Exakten Naturwissenschaften*, 1938.
Fröhlich, Heitler and Kemmer		*Proc. Roy. Soc.*, (A), 1938, **166**, 154–77.
Kemmer	..	*Ibid.*, 1938, **166**, 127–53.
Lovell	..	*Ibid.*, 1939, **172**, 568–82.
Massey and Corben	..	*Proc. Camb. Phil. Soc.*, 1939.
Proca	..	*J. Phys. Radium*, 1936, **7**, 347–53.
Stueckelberg	..	*Helv. phys. Acta*, 1938, **11**, 299–328.
Yukawa, Sakata and Taketani		*Proc. Phys. Math. Soc.*, Japan, 1938, **20**, 319–40.

[2] We wish to thank Dr. Lovell for sending us the manuscript of his paper.

Note added in Proof.—

In this paper reference was omitted to the note of Carmichael and Chou (*Nature*, 1939, **144**, 325). The experimental curves and the theoretical curve for spin $\frac{1}{2}$ are given in this Note. The theoretical curve for spin 1 coincides almost exactly in slope and absolute magnitude with the experimental tube station curve.

ON THE OCCURRENCE OF OVERTONE LINES IN RAMAN EFFECT

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(From the Department of Physics, Andhra University, Waltair)

Received September 9, 1939

1. *Harmonic Oscillator*

The theory of vibrational Raman scattering has been developed by a number of earlier workers and it is now generally recognised that the overtone lines, if at all they occur in Raman spectra, should ordinarily be very weak.* Placzek's work[1] contains a complete account of these and other important features relating to vibrational Raman lines. The relevant steps in the theory will be briefly given here. The polarisability of a molecule may be expanded as a series in the following manner :—

$$\alpha(q) = \alpha_0 + \sum_j \left(\frac{\partial \alpha}{\partial q_j}\right)_0 q_j + \tfrac{1}{2} \sum_{jk} \left(\frac{\partial^2 \alpha}{\partial q_j \, \partial q_k}\right)_0 q_j \, q_k + \cdots \qquad (1)$$

One special feature of this series is that only the limiting values of the derivatives pertaining to $q \to 0$ appear as the coefficients. The second and higher order derivatives under these conditions are likely to be quite negligible and the series may ordinarily be regarded as terminating with the second term. The q's are the normal co-ordinates and they are so chosen that each one of them is zero when the molecule is in its equilibrium configuration. A set of values for the q's will define a configuration q of the molecule. The matrix element $\alpha_{vv'}$ will be given by (2)

$$\alpha_{vv'} = \int \psi_{v'}^{*}(q) \, \alpha(q) \, \psi_v(q) \, dq. \qquad (2)$$

Let us, for simplicity, confine ourselves to diatomic molecules although results similar to those set forth below may easily be obtained for polyatomic molecules also. In such a case, there is only one degree of vibrational freedom to be considered and the change in the nuclear distance measured from the equilibrium value may be taken to represent the corresponding normal co-ordinate. If the molecule in question is regarded

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* This statement does not apply to cases where overtones occur with unusually large intensities as a result of what has been termed '*accidental degeneracy*'.

[1] *Handbuch der Radiologie*, 1934, **6**, 205.

as an ideal harmonic oscillator, the ψ's in (2) are real and represent the well-known eigen-functions of a harmonic oscillator involving the Hermite polynomials. Substituting the series (1) for $\alpha\,(q)$ in (2), the integration for specific values of v and v' may easily be performed by making use of the known properties of the Hermite polynomials. We have

$$a_{01} = c^{\frac{1}{2}}\left(\frac{\partial a}{\partial q}\right)_0\,;\; a_{02} = \frac{c}{\sqrt{2}}\left(\frac{\partial^2 a}{\partial q^2}\right)_0, \tag{3}$$

where $c = h/8\pi^2\nu_0\mu$, μ is the reduced mass and ν_0 is the vibration frequency. In (3), only the first term has been retained in each of the cases and the others are omitted as they are relatively insignificant. The squares of a_{01} and a_{02} will respectively determine the intensities of the fundamental and the overtone. If, as has been explained in the beginning, the second order derivative of the polarisability is zero or negligibly small, the overtone line will be of either zero or negligibly low intensity. It is the purpose of the present paper to show that on the contrary, even if the series in (1) terminates with the second term, we should expect the overtone line to occur with a finite intensity on account of the fact that all diatomic molecules are in reality anharmonic oscillators. If we take this fact into account, it may easily be shown that a term involving the first derivative $\left(\frac{\partial a}{\partial q}\right)_0$ also is present in the expression for a_{02}.

2. *Anharmonic Oscillator*

It has been shown by Morse[2] that the nuclear potential energy of various molecules is more satisfactorily represented by (4) than by the simple law appropriate to a harmonic oscillator

$$\mathrm{U}\,(r) = \mathrm{D}\,\{e^{-2a\,(r-r_0)} - 2e^{-a\,(r-r_0)}\}. \tag{4}$$

r_0 is the equilibrium nuclear distance and r is a particular value. This leads to the eigen-values

$$\mathrm{E}_n = h\nu_0\,(n + \tfrac{1}{2}) - h\nu_0 x\,(n + \tfrac{1}{2})^2.$$

The corresponding eigen-functions are no longer functions of Hermite polynomials but they involve the generalized Laguerre polynomials. If the radial part of the eigen-function is written as $1/r\;\mathrm{R}_n\,(r)$, we have[3]

$$\mathrm{R}_n\,(r) = \mathrm{A}_n\,e^{-(k/2)\,e^{-a\,(r-r_0)}}\,[ke^{-a\,(r-r_0)}]^{\frac{(k-2n-1)}{2}}\cdot \mathrm{L}_{kn}\,(ke^{-a\,(r-r_0)}) \tag{5}$$

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[2] E. U. Condon and P. M. Morse, *Quantum Mechanics*, 1929.

[3] J. L. Dunham, *Phys. Rev.*, 1929, **34**, 438.

where $K = 4\pi (2\mu D)^{\frac{1}{2}}/ah$ and $L_{kn}(ke^{-a(r-r_0)})$ is a polynomial in $(ke^{-a(r-r_0)})$ defined by

$$L_{kn}(x) = x^n - n(k-n-1)x^{n-1} + \tfrac{1}{2}n(n-1)(k-n-1)(k-n-2)x^{n-2}.$$

A_n is given by

$$A_n = \left[\frac{a(k-2n-1)}{n!(k-n-1)\ \Gamma(k-n-1)}\right]^{\frac{1}{2}}.$$

The constants a and k are given by

$$a = (8\pi^2 \mu\ \nu_0 x/h)^{\frac{1}{2}}; \quad k = \frac{1}{x}.$$

The matrix element $a_{vv'}$ will now be given by (6)

$$a_{vv'} = \int R_{v'}\, a(q)\, R_v\, dr. \tag{6}$$

Regarding the series (1) as terminating with the second term only and substituting for $a(q)$, we have since $dr = dq$

$$a_{01} = \left(\frac{\partial a}{\partial q}\right)_0 \int R_1 R_0\, q dq\,; \quad a_{02} = \left(\frac{\partial a}{\partial q}\right)_0 \int R_2 R_0\, q dq. \tag{7}$$

A method of evaluating these integrals has been given by Dunham.[3] Adopting the same procedure, we obtain

$$a_{01} = \left(\frac{\partial a}{\partial q}\right)_0 \cdot \frac{A_0 A_1}{a^2}\ \Gamma(k-1)\left\{\log\frac{k}{k-1\frac{1}{2}} - \log\frac{k}{k-2\frac{1}{2}}\right\}$$

$$a_{02} = \left(\frac{\partial a}{\partial q}\right)_0 \cdot \frac{A_0 A_2}{a^2}\ \Gamma(k-1)\left\{\log\frac{k}{k-1\frac{1}{2}} - 2\frac{k-3}{k-2}\log\frac{k}{k-2\frac{1}{2}} + \frac{k-4}{k-2}\log\frac{k}{k-3\frac{1}{2}}\right\}. \tag{8}$$

A further simplification by substituting the values of A_0, A_1 and A_2 in (8) will lead to (9)

$$a_{01} = \left(\frac{\partial a}{\partial q}\right)_0 \cdot \frac{(k-3)^{\frac{1}{2}}}{a}\left[\log\frac{k}{k-1\frac{1}{2}} - \log\frac{k}{k-2\frac{1}{2}}\right]$$

$$a_{02} = \left(\frac{\partial a}{\partial q}\right)_0 \cdot \frac{[(k-5)(k-2)]^{\frac{1}{2}}}{\sqrt{2}\cdot a}\left[\log\frac{k}{k-1\frac{1}{2}} - 2\frac{k-3}{k-2}\log\frac{k}{k-2\frac{1}{2}} + \frac{k-4}{k-2}\log\frac{k}{k-3\frac{1}{2}}\right]. \tag{9}$$

Thus we see that a_{02} survives even if the second order derivative of the polarisability with respect to the normal co-ordinate does not exist. In order to calculate the relative intensities of the fundamental and overtone Raman lines, it is only necessary to substitute the numerical values of a and k in (9) and obtain the squares of a_{01} and a_{02}. The results so

obtained in the case of a few common molecules are given in the next section. It may be remarked here that if the anharmonicity constant x is very small, k is very large and (9) reduces in the limit to (10).

$$a_{01} = \frac{1}{a\,k^{\frac{1}{2}}} \left(\frac{\partial a}{\partial q}\right)_0 ; \quad a_{02} = 0. \tag{10}$$

As may be expected, these agree with the values directly derived for an ideal harmonic oscillator on the assumption that the third and the higher terms in (1) are absent.

3. *Application to Some Common Molecules*

Taking the known spectroscopic constants,[4] a_{01} and a_{02} have been calculated and given in Table I for some simple cases of diatomic molecules. The intensities of the corresponding Raman lines are in the ratio of $\nu_f{}^4 a_{01}{}^2 : \nu_h{}^4 a_{02}{}^2$, where ν_f and ν_h are respectively the frequencies of the fundamental and overtone Raman lines. These depend to some extent on the position of the exciting line and the figures given in the last column of Table I have been obtained on the assumption that the fundamental as well as the overtone line under comparison are excited by λ 3650 A.U.

TABLE I

Molecule	$\mu \times 10^{24}$	$\nu_0 x$† (cm.$^{-1}$)	ν_0† (cm.$^{-1}$)	K	$a \times 10^{-8}$	$a_{01} \times 10^{10}$	$a_{02} \times 10^{11}$	$\frac{a_{01}{}^2}{a_{02}{}^2}$	$\frac{\nu_f{}^4 \times a_{01}{}^2}{\nu_h{}^4 \times a_{02}{}^2}$
HCl ..	1·615	51·90	2939·7	57·605	1·741	7·63	7·23	111	180
HBr ..	1·641	44	2647·0	60·16	1·616	8·04	7·46	116	176
H_2 ..	0·831	113·5	4371·0	38·511	1·847	8·83	10·3	74	155
N_2 ..	11·54	14·445	2359·6	163·35	2·455	3·19	1·77	325	478
O_2 ..	13·19	11·645	1584·9	136·10	2·354	3·65	2·23	268	342

† The proper value to be used in calculating a is obtained by multiplying the figure in this column by the velocity of light.

It will be noted that the intensity of the fundamental is about 150 to 500 times that of the overtone in the set of molecules studied. This is an upper limit as we have assumed that $\left(\frac{\partial^2 a}{\partial q^2}\right)_0$ does not exist. In a case where this term also exists, the overtone will have a larger intensity. Intense exposures with a view to record the overtone lines and check the theory of anharmonic oscillators have not so far been given. The case of

[4] W. Jevons, *Report on Band Spectra of Diatomic Molecules*, 1932.

hydrogen is particularly encouraging and it should be quite possible to record the overtone at approximately double the normal Raman shift as its intensity is expected to be only $\frac{1}{155}$ of that of the fundamental.

It is possible to extend these ideas in a semi-empirical manner to more complicated molecules in order to explain the occurrence of overtone lines in their Raman spectra. This work along with a fuller discussion of the available experimental results in such cases will be taken up in a separate communication.

NOTE ON SOME FORMULÆ INVOLVING THE LAGUERRE AND HERMITIAN POLYNOMIALS AND BESSEL FUNCTIONS

By V. R. Thiruvenkata Char

(*Department of Mathematics, Central College, Bangalore*)

Received September 2, 1939

(Communicated by Prof. B. S. Madhava Rao)

§ 1. The purpose of this note is to give simple derivations of some well-known formulæ involving the Laguerre and the Hermitian polynomials and Bessel functions. Incidentally some further relations are derived which appear to be new.

§ 2. The generalised Laguerre polynomial $L_n^{(a)}(x)$ is defined by

$$L_n^{(a)}(x) = \frac{e^x x^{-a}}{n!} \frac{d^n}{dx^n} (e^{-x} x^{n+a}) \tag{1}$$

and satisfies the orthogonality relations :

$$\int_0^\infty e^{-t} t^a L_n^{(a)}(t) L_m^{(a)}(t) dt = \begin{cases} 0, & n \neq m \\ \dfrac{\Gamma(n+a+1)}{n!}, & n = m. \end{cases} \tag{2}$$

By direct integration by parts we get

$$\int_0^\infty e^{-t} t^{m+a} L_n^{(a)}(t) dt = \begin{cases} 0, & m < n \\ \dfrac{(-1)^n m!}{n!\,(m-n)!} \Gamma(m+a+1), & m \geqslant n \end{cases} \tag{3}$$

From this we immediately derive by term-by-term integration[1]

$$\int_0^\infty e^{-t} t^{a/2} J_a(2\sqrt{xt}) L_n^{(a)}(t) dt = \frac{e^{-x} x^{n+\frac{a}{2}}}{n!}. \tag{4}$$

Applying the Fourier-Bessel integral theorem we get Wigert's formula

$$L_n^{(a)}(x) = \frac{e^x x^{-\frac{a}{2}}}{n!} \int_0^\infty e^{-t} t^{n+\frac{a}{2}} J_a(2\sqrt{xt}) dt \tag{5}$$

[1] This is easily justified. A similar remark is to be understood with reference to other inversions of limit-processes occurring throughout the paper.

If we now assume

$$t^{-\frac{\alpha}{2}} J_\alpha (2\sqrt{xt}) = \sum_0^\infty a_n (x) L_n^{(\alpha)} (t)$$

we get using (2) and (4)

$$\frac{\Gamma (n + \alpha + 1)}{n!} a_n (x) = \frac{e^{-x} x^{n + \frac{\alpha}{2}}}{n!}$$

We thus get Hille's generating function for $L_n^{(\alpha)} (x)$:

$$\Sigma \frac{L_n^{(\alpha)} (t)}{\Gamma (n + \alpha + 1)} x^n = e^x (xt)^{-\frac{\alpha}{2}} J_\alpha (2\sqrt{xt}) \quad (\alpha > -1) \tag{6}$$

§3. If we put $n = 0$ in (4) we get

$$\int_0^\infty e^{-t} x^{\frac{\alpha}{2}} J_\alpha (2\sqrt{xt})\, dt = e^{-x} x^{\frac{\alpha}{2}}$$

or setting $2\sqrt{xt} = au$, $a^2/4x = p^2$, this becomes

$$\int_0^\infty e^{-p^2u^2} J_\alpha (au)\, u^{\alpha+1}\, du = \frac{a^\alpha}{(2p^2)^{\alpha+1}} \exp\left(-\frac{a^2}{4p^2}\right) \tag{7}$$

which is Weber's first exponential integral.[2]

Again from (6) we have

$$\sum_n \frac{L_n^{(\alpha)} (t)}{\Gamma (n + \alpha + 1)} x^n = e^x (xt)^{-\frac{\alpha}{2}} J_\alpha (2\sqrt{xt})$$

$$\sum_m \frac{L_m^{(\alpha)} (t)}{\Gamma (m + \alpha + 1)} y^m = e^y (yt)^{-\frac{\alpha}{2}} J_\alpha (2\sqrt{yt}).$$

Multiplying the two series we get

$$\sum_n \{L_n^{(\alpha)} (t)\}^2 \frac{x^n y^n}{\{\Gamma (n + \alpha + 1)\}^2}$$

$$+ \sum'_{m,n} \frac{L_n^{(\alpha)} (t)\, L_m^{(\alpha)} (t)}{\Gamma (n+\alpha+1)\, \Gamma (m+\alpha+1)} x^n y^m = e^{x+y} (xyt^2)^{-\frac{\alpha}{2}} J_\alpha(2\sqrt{xt}) J_\alpha(2\sqrt{yt}).$$

Multiplying by $e^{-t} t^\alpha$ and integrating from 0 to ∞ we get

$$\sum_n \frac{(xy)^n}{n!\, \Gamma (n + \alpha + 1)} = e^{x+y} (xy)^{-\frac{\alpha}{2}} \int_0^\infty e^{-t} J_\alpha (2\sqrt{xt})\, J_\alpha (2\sqrt{yt})\, dt.$$

Put $2x = a^2/2p^2$, $2y = b^2/2p^2$, $2t = 2p^2u^2$. We then get

$$\Sigma \frac{(ab/4p^2)^{\alpha+2n}}{n!\, \Gamma (n + \alpha + 1)} = 2p^2 \cdot \exp\left(\frac{a^2 + b^2}{4p^2}\right) \int_0^\infty e^{-p^2u^2} J_\alpha (au)\, J_\alpha (bu)\, udu$$

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[2] Watson, *Bessel Functions*, pp. 394–95.

or

$$\int_0^\infty e^{-p^2u^2}\, J_a(au)\, J_a(bu)\, u\,du = \frac{1}{2p^2}\exp\left(-\frac{a^2+b^2}{4p^2}\right) I_a\left(\frac{ab}{2p^2}\right) \qquad (8)$$

which is Weber's second exponential integral.[2]

§ 4. Now consider the integral

$$\int_0^\infty e^{-\frac{tx}{1-x}}\cdot e^{-t}\, t^a\, L_n^{(a)}(t)\, dt.$$

By (5) this is equal to

$$\frac{1}{n!}\int_0^\infty e^{-kt}\, t^{\frac{a}{2}}\, dt \int_0^\infty e^{-u}\, u^{n+\frac{a}{2}}\, J_a(2\sqrt{tu})\, du,\ k = \frac{x}{1-x}$$

$$= \frac{1}{n!}\int_0^\infty e^{-u}\, u^{n+\frac{a}{2}}\, du \int_0^\infty e^{-kt}\, t^{\frac{a}{2}}\, J_a(2\sqrt{tu})\, dt.$$

Setting $2t = \xi^2$, $2u = v^2$, $2\sqrt{ut} = \xi v$, this becomes

$$\frac{1}{n!}\frac{1}{2^{n+a}}\int_0^\infty e^{-\frac{v^2}{2}}\, v^{2n+a+1}\, dv \int_0^\infty e^{-\frac{1}{2}k\xi^2}\, J_a(\xi v)\, \xi^{a+1}\, d\xi$$

$$= \frac{1}{n!}\frac{1}{2^{n+a}}\frac{1}{k^{a+1}}\int_0^\infty e^{-\frac{v^2}{2}\left(1+\frac{1}{k}\right)}\, v^{2n+2a+1}\, dv, \text{ by (7)}$$

$$= (1-x)^{a+1}\cdot\frac{x^n}{n!}\,\Gamma(n+a+1).$$

Thus[3]

$$\int_0^\infty e^{-\frac{tx}{1-x}}\cdot e^{-t}\, t^a\, L_n^{(a)}(t)\, dt = (1-x)^{a+1}\,\frac{\Gamma(n+a+1)}{n!}\,x^n. \qquad (9)$$

Now assume :

$$e^{-\frac{tx}{1-x}} = \Sigma\, a_n(x)\, L_n^{(a)}(t).$$

We then find, using (9), $a_n(x) = x^n(1-x)^{a+1}$.

Thus

$$\Sigma\, L_n^{(a)}(t)\cdot x^n = \frac{e^{-\frac{xt}{1-x}}}{(1-x)^{a+1}} \qquad (a > -1) \qquad (10)$$

which is the ordinary generating function for $L_n^{(a)}(x)$.

§ 5. The Hermitian polynomials are defined by

$$e^{-x^2}\, H_n(x) = \frac{d^n}{dx^n}(e^{-x^2}).$$

[3] This result may however be obtained more simply by directly using (1).

By direct integration by parts we find

$$\left.\begin{aligned}\int_{-\infty}^{+\infty} e^{-t^2} H_{2n+1}(t) \cos 2xt\, dt &= 0\\ \int_{-\infty}^{+\infty} e^{-t^2} H_{2n}(t) \cos 2xt\, dt &= (-1)^n (2x)^{2n} \sqrt{\pi}\, e^{-x^2}\end{aligned}\right\} \tag{11}$$

$$\left.\begin{aligned}\int_{-\infty}^{+\infty} e^{-t^2} H_{2n}(t) \sin 2xt\, dt &= 0\\ \int_{-\infty}^{+\infty} e^{-t^2} H_{2n+1}(t) \cos 2xt\, dt &= (-1)^{n+1} (2x)^{2n+1} \sqrt{\pi}\, e^{-x^2}\end{aligned}\right\} \tag{12}$$

If we now assume

$$\cos 2xt = \Sigma\, a_n(x)\, H_n(t), \text{ we find } a_{2n+1} = 0,\ a_{2n} = (-1)^n \cdot \frac{e^{-x^2} x^{2n}}{(2n)!}.$$

$$\left.\begin{aligned}\text{Thus} \qquad e^{x^2} \cos 2xt &= \Sigma\, (-1)^n \frac{H_{2n}(t)}{(2n)!}\, x^{2n}\\ \text{Similarly} \qquad e^{x^2} \sin 2xt &= \Sigma\, (-1)^{n+1} \frac{H_{2n+1}(t)}{(2n+1)!}\, x^{2n+1}\end{aligned}\right\} \tag{13}$$

which may be considered as alternative generating functions for $H_n(x)$. In particular for $x = 1$ we obtain the known relations[4]

$$\left.\begin{aligned}\Sigma\, (-1)^n \frac{H_{2n}(t)}{(2n)!} &= e \cos 2t\\ \Sigma\, (-1)^n \cdot \frac{H_{2n+1}(t)}{(2n+1)!} &= -e \sin 2t\end{aligned}\right\} \tag{14}$$

Again in the formulæ (13) replace x by $\sqrt{x}$, t by $\sqrt{t}$, we get

$$\left.\begin{aligned}e^x \cos(2\sqrt{xt}) &= \Sigma\, (-1)^n \cdot \frac{H_{2n}(\sqrt{t})}{(2n)!}\, x^n\\ x^{-\frac{1}{2}} e^x \sin(2\sqrt{xt}) &= \Sigma\, (-1)^{n+1} \frac{H_{2n+1}(\sqrt{t})}{(2n+1)!}\, x^n\end{aligned}\right\}. \tag{15}$$

Also if in (6) we take $\alpha = -\frac{1}{2}$ and $+\frac{1}{2}$ respectively we get

$$\left.\begin{aligned}\Sigma \frac{L_n^{(-\frac{1}{2})}(t)}{\Gamma(n+\frac{1}{2})}\, x^n &= e^x (xt)^{\frac{1}{4}} J_{-\frac{1}{2}}(2\sqrt{xt}) = \frac{e^x}{\sqrt{\pi}} \cos(2\sqrt{xt})\\ \Sigma \frac{L_n^{(\frac{1}{2})}(t)}{\Gamma(n+\frac{3}{2})}\, x^n &= e^x (xt)^{-\frac{1}{4}} J_{\frac{1}{2}}(2\sqrt{xt}) = e^x \cdot \frac{(xt)^{-\frac{1}{2}}}{\sqrt{\pi}} \sin(2\sqrt{xt})\end{aligned}\right\} \tag{16}$$

[4] Doetsch, *Theorie u. Anwendung der Laplace-transformation*, p. 185.

Comparing (15) and (16) we get Szegö's well-known relations

$$\left.\begin{aligned} \mathrm{H}_{2n}(\sqrt{t}) &= (-1)^n\, 2^{2n}\cdot n!\, \mathrm{L}_n^{(-\frac{1}{2})}(t) \\ \mathrm{H}_{2n+1}(\sqrt{t}) &= (-1)^{n+1}\, 2^{2n+1}\cdot n!\, t^{\frac{1}{2}}\, \mathrm{L}_n^{(\frac{1}{2})}(t) \end{aligned}\right\} \tag{17}$$

§ 6. Now take $\alpha = -\frac{1}{2}$ in (10) and use (17). We get, after interchanging x and t and writing x^2 and t^2 in place of x and t,

$$\Sigma(-1)^n \frac{\mathrm{H}_{2n}(x)}{2^{2n}\cdot n!}\cdot t^{2n} = \frac{e^{-\frac{t^2x^2}{1-t^2}}}{\sqrt{1-t^2}}.$$

Multiplying by $e^{-x^2}\,\mathrm{H}_{2n}(x)$ and integrating from $-\infty$ to $+\infty$ we get

$$\int_{-\infty}^{+\infty} \frac{e^{-\frac{x^2}{1-t^2}}}{\sqrt{1-t^2}}\,\mathrm{H}_{2n}(x)\,dx = (-1)^n\cdot\sqrt{\pi}\cdot\frac{(2n)!}{n!}\,t^{2n}$$

or writing $s = 1/(1-t^2)$, this becomes

$$\int_{-\infty}^{+\infty} e^{-sx^2}\,\mathrm{H}_{2n}(x)\,dx = \sqrt{\pi}\cdot\frac{(2n)!}{n!}\,\frac{(1-s)^n}{s^{n+\frac{1}{2}}}. \tag{18}$$

Similarly, we get

$$\int_{-\infty}^{+\infty} e^{-sx^2}\,\mathrm{H}_{2n+1}(x)\,x\,dx = -\sqrt{\pi}\cdot\frac{(2n+1)!}{n!}\,\frac{(1-s)^n}{s^{n+\frac{3}{2}}} \tag{19}$$

These formulæ were obtained by Doetsch[5] in a different way.

§ 7. We can write (4) in the form

$$\int_0^{\infty} e^{-t}\,t^{\frac{\alpha}{2}}\,\mathrm{L}_n^{(\alpha)}(t)\,x^{\frac{\alpha}{2}}\,\mathrm{J}_\alpha(2\sqrt{xt})\,dt = \frac{e^{-x}\,x^{n+\alpha}}{n!}.$$

Differentiating n times w.r.t. x, and using the relation

$$\left(\frac{d}{zdz}\right)^m\{z^p\,\mathrm{J}_p(z)\} = z^{p-m}\,\mathrm{J}_{p-m}(z)$$

we get

$$\int_0^{\infty} e^{-t}\,t^{\frac{n+\alpha}{2}}\,\mathrm{L}_n^{(\alpha)}(t)\,\mathrm{J}_{\alpha-n}(2\sqrt{xt})\,dt = e^{-x}\,x^{\frac{n+\alpha}{2}}\,\mathrm{L}_n^{(\alpha)}(x) \tag{20}$$

Changing α into $2\alpha + n$, this takes the form

$$\int_0^{\infty} e^{-t}\,t^{n+\alpha}\,\mathrm{L}_n^{(2\alpha+n)}(t)\,\mathrm{J}_{2\alpha}(2\sqrt{xt})\,dt = e^{-x}\,x^{n+\alpha}\,\mathrm{L}_n^{(2\alpha+n)}(x)\quad(\alpha > -\tfrac{1}{2}) \tag{21}$$

which is similar to Watson's integral equation[6] for $\{\mathrm{L}_n^{(\alpha)}(x)\}^2$.

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[5] Doetsch, *Math. Zeit.*, **32**, 587–99.

[6] Watson, *Journ. L.M.S.*, 1936, **11**, No. 44, Part 4, 256.

We may write (20) also in the form

$$2\int_0^{-\infty} e^{-t^2}\, t^{n+a+1}\, L_n^{(a)}(t^2)\, J_{a-n}(2xt)\, dt = e^{-x^2}\, x^{n+a}\, L_n^{(a)}(x^2). \tag{22}$$

By taking $a = -\frac{1}{2}$ and $+\frac{1}{2}$ in (22) we get the relations

$$\left.\begin{aligned} \int_{-\infty}^{+\infty} e^{-t^2}\, t^{n+\frac{1}{2}}\, H_{2n}(t)\, J_{-n-\frac{1}{2}}(2xt)\, dt &= e^{-x^2}\, x^{n-\frac{1}{2}}\, H_{2n}(x) \\ \int_{-\infty}^{+\infty} e^{-t^2}\, t^{n+\frac{1}{2}}\, H_{2n+1}(t)\, J_{-n+\frac{1}{2}}(2xt)\, dt &= e^{-x^2}\, x^{n-\frac{1}{2}}\, H_{2n+1}(x) \end{aligned}\right\} \tag{23}$$

THE CRYSTAL DIAMAGNETISM OF TELLURIUM

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1. Introduction

The magnetic properties of single metal crystals has assumed considerable interest and importance in recent years. From the known magnetic susceptibilities of the crystal in different directions, it is possible to fix the nature of binding of the valence electrons in different directions.

McLennan and his associates[1] found the magnetic susceptibilities of crystals of zinc, cadmium, antimony and tin. Focke[2] prepared bismuth crystals with desired orientations and found the principal susceptibilities of this metal. Goetz and Focke[3] studied the effects of added impurities on the magnetic anisotropy of bismuth crystal. Vogt[4] found that solid mercury possesses a small anisotropy. Hoge[5] determined the susceptibilities of white tin crystals along and normal to the tetragonal axis. Hart[6] investigated the properties of antimony crystals.

Schoenburg and Uddin[7] measured the magnetic anisotropy of bismuth crystals and showed that even 0·1% of tin or tellurium produces a large difference in the anisotropy. Rao and Sriraman[8] investigated cadmium crystals and Rao and Subramaniam[9] and later Rao and Narayanaswamy[10] undertook a careful study of the principal susceptibilities of thallium crystals.

Tellurium is an element of great interest from several points of view. The investigations of Honda[11] gave for its mass susceptibility the value $-0{\cdot}32$.* Its atomic susceptibility therefore becomes $-41{\cdot}8$. Kido[12] found for the ionic susceptibility of tellurium (Te^{+6}) the value of $-4{\cdot}5$. The susceptibility of the element is thus seen to be due almost entirely to the susceptibility of the six valence electrons.

Tellurium exhibits several characters of a metal. It is a silver-white metal which when crystallized gives rise to cleavage faces of beautiful

* All susceptibilities in this paper are given in 10^{-6} units.

metallic lustre. Its electrical and thermal conductivities distinguish it as a metal. But in several chemical reactions, tellurium shows the behaviour of a non-metal.

The element shows an abnormally high Hall effect. The temperature variation of this effect led Wold[13] to suggest the existence of two crystalline forms, the α-variety, stable below 354° C., and the β-variety, stable above this temperature.

In this investigation, the principal susceptibilities of tellurium single crystals have been determined. The effect of temperature on the susceptibility was studied in the range 30° C.–500° C. The changes of anisotropy produced by small admixtures of foreign metals have been carefully investigated.

2. *Crystal Structure*

Slattery[14] found that tellurium crystallizes in a simple triangular lattice with three atoms associated with each point on the lattice. The side a of the basal triangle was fixed by him as 4·44 Å and the height between the two lattice planes as 5·912 Å. The axial ratio becomes 1·33 and the density 6·25.

The structure of tellurium has been worked out in a very thorough manner by Bradley[15] using the crystal powder method. The structure was found to be simple rhombohedral with interaxial angles of almost 90°, in which each atom is slightly displaced towards two of the six adjacent atoms. The resulting structure is a threefold spiral, consisting of three interpenetrating simple triangular lattices. Each atom is exactly above the third atom below in the helix.

Fig. 1 gives the projection of the system, the trigonal axis being perpendicular to the plane of the paper. Differently shaded circles represent atoms at different levels along the trigonal axis. The radius r of the helix is 1·20 Å. The shortest distance between the atoms in the same helix (2·86 Å) is less than the shortest distance between the atoms in different helices. Hence the atoms in the same helix are held together by greater cohesive forces than those binding atoms in different helices. The trigonal axis is therefore unique. It accounts for many of the directional properties of crystalline tellurium. Clark[16] gives for the edge lengths a and c of the hexagonal lattice of tellurium the values of 4·495 Å and 5·912 Å.

One would expect that the magnetic susceptibility along the trigonal axis to be different from the value at right angles to this axis. The magnetic anisotropy however is found to be small in the case of tellurium.

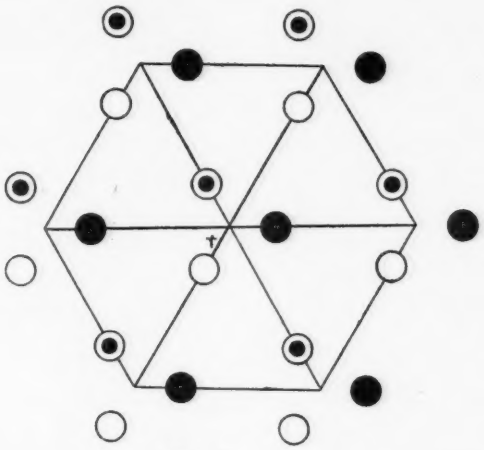

FIG. 1

Effects due to temperature and additions of small quantities of foreign metals tend to decrease this anisotropy.

3. *Experiment*

Preparation of Crystals—

Full details of the preparation of polycrystalline and single crystal rods of metal have been given in previous papers.[17]

The pyrex glass tubes in which the rods were formed were initially calibrated with water. The tube used was about 20 cm. long and had an internal diameter of about 4 mm. Half the length of the tube was filled with molten metal *in vacuo*.

The single crystals were prepared by the method of slow cooling using an electrical furnace at 500° C. to melt the metal. The tube containing the metal was lowered through the furnace at a speed of about 2 cm. per hour. The crystals prepared in this manner were broken open at the end of the magnetic experiments. Perfect cleavage faces were obtained. These crystals are known to cleave easily along the 211 plane.

The alloys were prepared by mixing together weighed quantities of the metals in vacuum and running the molten alloy down the experimental tube. About half the tube was filled with the alloy and the tube was sealed in such a manner that the lengths of the glass tube above and below the metal surface were nearly the same.

The Gouy Method—

The magnetic susceptibility of the metal was determined by the Gouy method. The tubes were weighed with and without the magnetic field.

Let mg be the Gouy force when the tube contains the solid and $m'g$ the Gouy force when the tube contains water. If K_m and K_w are the volume susceptibilities of the metal and water respectively, it may be shown that

$$K_m = K_w \times \frac{mg}{m'g}.$$

The volume susceptibility of water is assumed to be $-0{\cdot}720$ at 30° C. If d is the density of the metal, the mass susceptibility is given by

$$\chi = \frac{K_m}{d} = \frac{0{\cdot}720}{d} \cdot \frac{m}{m'}.$$

By making the lengths of the glass above and below the metal surface the same, compensation for the glass is secured. There is also compensation for the susceptibility of the air displaced.

It is well known that metals cooled rapidly or slowly are not always perfect polycrystals. They are often found to possess preferred orientations, which give them directional properties. A perfect polycrystal should not show any such directional properties. Ordinary metal rods may be converted into perfect polycrystals by annealing them for several hours at temperatures slightly lower than their melting points and subsequent slow cooling. In the case of tellurium, the rods were annealed for four hours at 420° C. and cooled slowly to attain the room temperature in about three hours. The same procedure was adopted in the case of tellurium alloyed with small quantities of foreign metals.

Measurement of the Principal Susceptibilities of Single Crystals—

Measurements of the Gouy force on the crystal were made at different positions when the crystal was rotated. The forces were measured at intervals of 30°.

When the Gouy forces are plotted against the orientation readings, maxima and minima occurred alternately at intervals of 90°. The crystal was next placed in each of these positions and the Gouy forces were determined for different field currents.

If $\chi_{\parallel}$ and $\chi_{\perp}$ be the susceptibilities parallel and perpendicular to the trigonal axis, it may be shown that

$$\chi_{\perp} = \chi_{90}$$

$$\text{and } \chi_{\parallel} = \frac{\chi_0 - \chi_{90}\cos^2\phi}{\sin^2\phi},$$

where χ_0 and χ_{90} are the susceptibilities corresponding to the maximum and minimum Gouy force and ϕ is the angle between the axis of the rod and the trigonal axis of the crystal.

It is seen that $\chi_\perp$ is directly given by the minimum specific susceptibility of the crystal. To find $\chi_\parallel$, χ_0 and ϕ should also be known.

The most accurate method of determining ϕ is by using X-rays. In the absence of proper equipment, the following method was adopted. If the single crystal sealed within the tube is converted into a perfect polycrystal, the susceptibility χ is given by

$$\chi = \tfrac{1}{3}\,(2\chi_\perp + \chi_\parallel).$$

If χ and $\chi_\perp$ are known, the value $\chi_\parallel$ may easily be determined.

4. *Results*

(*a*) *Polycrystalline Metal*—

The susceptibility of pure polycrystalline tellurium was determined by measuring the Gouy force on two specimen rods. Each of these rods was annealed successively thrice and after each annealing the magnetic observations were made. The results obtained with a typical specimen are shown in Table I.

The density of the metal was found by an accurate hydrostatic method to be 6·25 grams per c.c.

TABLE I

Current in amperes	The field strength in kilogauss	Gouy force on		K	χ
		Water	Tellurium		
		mg.	mg.		
3	13·6	8·5	22·7	−1·923	−0·3077
4	17·0	13·4	35·7	−1·918	−0·3069
5	19·5	17·5	46·7	−1·922	−0·3075
6	20·6	19·6	52·3	−1·921	−0·3073
7	21·3	21·0	56·1	−1·923	−0·3077
			Mean	−1·921	−0·3074

It will be observed that the mass susceptibility is independent of the magnetic field intensity showing the absence of any ferromagnetic impurity in the metal.

The results obtained with the six measurements made with two specimen rods are given in Table II.

TABLE II

Serial No.	χ
1	$-0{\cdot}3074$
2	$-0{\cdot}3080$
3	$-0{\cdot}3090$
4	$-0{\cdot}3085$
5	$-0{\cdot}3093$
6	$-0{\cdot}3118$
Mean	$-0{\cdot}309$

The measurements obtained by other investigators are collected in Table III for comparison.

TABLE III

Investigators	χ
Curie[18] ..	$-0{\cdot}303$
McLennan and Cohen[19] ..	$-0{\cdot}308$
Honda[11] ..	$-0{\cdot}320$
Pascal[20] ..	$-0{\cdot}297$
Bhatnagar and Dhawan[21] ..	$-0{\cdot}317$
Narayanaswamy (unpublished) ..	$-0{\cdot}298$
Authors ..	$-0{\cdot}309$

The agreement between the value obtained here and those of other investigators is quite satisfactory.

(*b*) *Principal Susceptibilities of Tellurium Single Crystals*—

In Table IV are shown the values of the Gouy force for various angles of setting (θ) during one complete rotation. The current through the electromagnet was maintained at 5 amperes during these measurements.

TABLE IV

Setting $\theta°$	Gouy force in mg.	Setting $\theta°$	Gouy force in mg.
0	48·4	210	48·2
30	48·1	240	47·5
60	47·6	270	46·9
90	47·0	300	47·5
120	47·4	330	48·0
150	47·9	360	48·5
180	48·5	..	..

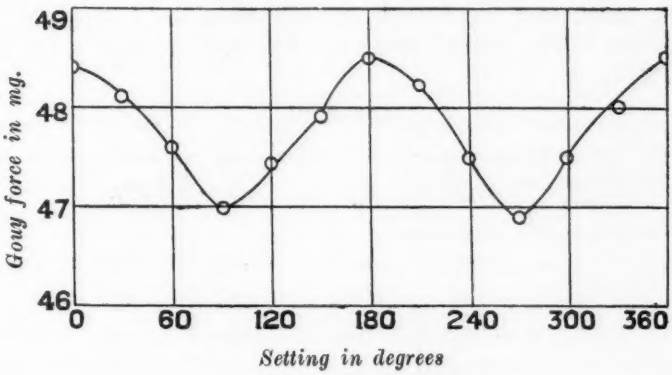

FIG. 2

The graph drawn between θ and the Gouy force is shown in Fig. 2. There are maxima and minima at intervals of 90°. The crystal was next placed successively at each of these positions and the Gouy forces determined for field currents of 3, 4, 5, 6 and 7 amperes.

The same specimen was next well annealed and the Gouy forces on the specimen determined for the same field currents. The minimum and maximum volume susceptibilities for a crystal specimen and the volume susceptibility of the same specimen in the polycrystalline state are tabulated.

TABLE V

Current in amps.	Gouy force on water in mg.	Minimum Gouy force on crystal in mg.	$K_{min.}$	Maximum Gouy force on crystal in mg.	$K_{max.}$	Gouy force on poly-crystal in mg.	$K_{poly.}$
3	8·3	21·5	− 1·865	22·3	− 1·934	22·4	− 1·943
4	13·3	34·0	− 1·841	35·1	− 1·900	35·4	− 1·922
5	17·3	44·5	− 1·852	46·1	− 1·919	46·2	− 1·923
6	19·4	49·7	− 1·845	51·3	− 1·904	51·5	− 1·911
7	20·7	53·2	− 1·850	54·9	− 1·909	55·2	− 1·916
		Mean	− 1·851	..	− 1·913	..	− 1·923

It is found that the volume susceptibilities are independent of the field currents. The results obtained with four crystals are shown in Table VI.

TABLE VI

Crystal Number	$K_{poly.}$	$K_{\perp}$	$K_{\parallel}$	$K_{\parallel}/K_{\perp}$ (Anisotropy)
1	− 1·923	− 1·851	− 2·067	1·12
2	− 1·921	− 1·843	− 2·077	1·13
3	− 1·913	− 1·856	− 2·027	1·09
4	− 1·920	− 1·847	− 2·066	1·12
Mean	− 1·92	− 1·85	− 2·06	1·11

The volume susceptibility of the poylcrystalline specimen $K_{poly.} = \frac{1}{3}(2K_{\perp} + K_{\parallel})$.

Since $K_{\perp} = K_{min.}$ for the crystal, the value of $K_{\perp}$ for each crystal is directly found from Table V. From a knowledge of the corresponding polycrystalline value, the volume susceptibility of the crystal parallel to the trigonal axis $K_{\parallel}$ may be calculated. We assume here that the density of the specimen in the crystalline form is the same as in the polycrystalline form. Measurements of densities made with the two forms of the metal gave identical values.

The principal mass susceptibilities of tellurium crystal are given below. They have been calculated from the mean values of Table VI, the density of the metal being as 6·25 gm. c.c.

TABLE VII

	Value
$\chi_{\perp}$	−0·296
$\chi_{\parallel}$	−0·329
χ_{poly}	−0·307
$\chi_{\parallel}/\chi_{\perp}$ (Anisotropy) ..	1·11

The magnetic anisotropy is found to be small. McLennan and Cohen[19] attempted to find the principal susceptibilities of tellurium crystals but they found no changes in the Guoy force as the crystal was rotated about its cylindrical axis. Since the anisotropy is small, it is likely that they did not observe the small variation. Some unpublished work by Narayanaswamy in this laboratory, gave for the anisotropy of tellurium the value of 1·03. It is likely that small impurities might have brought down the anisotropy to this value.

(c) *Influence of Temperatures*—

With the aid of an electric heater, the crystal was heated to about 500° C. and the principal susceptibilities of tellurium crystals were found at different intermediate temperatures. The electrical heating arrangement was similar to that adopted by Rao and Subramaniam.[9] The pole-pieces were cooled by several folds of muslin drenched frequently with iced water.

The temperature inside the electric heater was determined previously for different heating currents. These temperatures were found with a mercury thermometer up to 300° C. and a thermometer of platinum-rhodium couple at higher temperatures. It was estimated that above 100° C., the temperatures were correct to within 10°. For the slow variations observed in this investigation, this approximation was enough.

The results obtained are given in Table VIII. The values at any temperature are the mean of at least three measurements.

TABLE VIII

Temperature °C	$K_{poly.}$	$K_{\perp}$	$K_{\parallel}$	$K_{\parallel}/K_{\perp}$
30	−1·92	−1·85	−2·06	1·11
90	−1·90	−1·85	−2·00	1·08
160	−1·88	−1·85	−1·94	1·05
220	−1·85	−1·85	−1·85	1·00
300	−1·85	−1·85	−1·85	..
360	−1·85	−1·85	−1·85	..
410	−1·80	−1·80	−1·80	..
440	−1·70	−1·70	−1·70	..
480	−0·3	−0·3	−0·3	..
500	−0·25	−0·25	−0·25	..

It should be mentioned here that the glass surrounding the metal in the tube was at the temperature of the furnace while the glass above was at a much lower temperature. Further the air around the lower portion of the tube was also at a higher temperature than the air surrounding the upper portion. The volume susceptibility K_A of air varies inversely as the square of its absolute temperature. Hence the volume susceptibility decreases rapidly at higher temperatures.

Test experiments carried out with pyrex tubes (of the same lengths as those used for the crystals) which were evacuated and sealed, showed that the Gouy force on them never exceeded 0·2 mg. Since we are concerned more with the general nature of the temperature variation of magnetic susceptibility, this small factor of correction was not taken into account.

No attempt has been made to calculate the mass susceptibility at different temperatures, in view of the uncertainty of the density values. Further since the coefficient of linear expansion of pyrex glass is small, no account has been taken of the variation of its cross-section when the temperature is raised.

An examination of Table VIII and Fig. 3 in which the results are plotted, shows that as the temperature is raised, the volume susceptibility parallel to the principal axis decreases while the value normal to this axis remains constant. The magnetic anisotropy decreases also. At 220° C.

it is found that this anisotropy becomes equal to unity. The polycrystalline value also shows a decrease up to 220° C. and thereafter it has the same value as $\chi_{\perp}$ or $\chi_{\parallel}$.

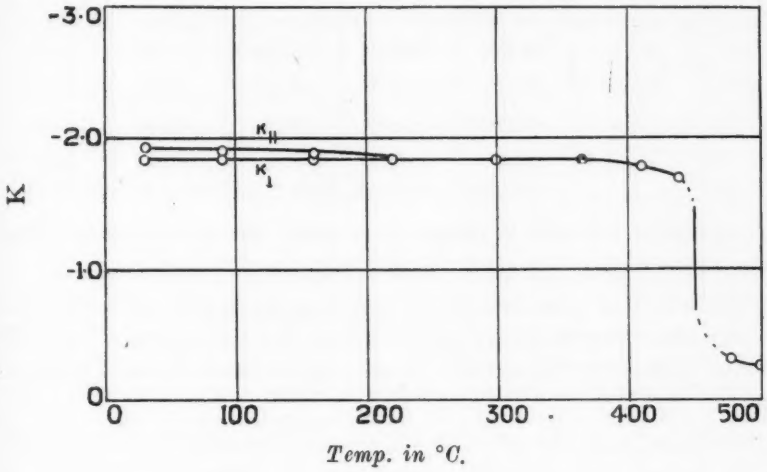

FIG. 3

At the melting point (450° C.) there is a large drop in the susceptibility value from 1·7 to 0·3.

These results agree with the conclusions of Honda[11] who studied the temperature variation of the mass susceptibility of tellurium. He found that the susceptibility remained practically constant from 18° up to the melting point. There was a sudden decrease to 0·071 at 470° C. and a further gradual decrease to 0·046 at 525° C.

What is of special interest in the present investigation is that the susceptibility parallel to the principal axis decreases while the value normal to this axis is constant. At 220° C., the metal appears magnetically isotropic.

(*d*) *Influences of Small Quantities of Foreign Metals*—

Lead.—The lead used was a pure Kahlbaum sample. Its specific susceptibility was found to be $-0·107$ by the Curie method. The results are given in Table IX.

TABLE IX

Specimen No.	% by weight of lead	Density in gm./c.c.	Mean χ	$\chi_\perp$	$\chi_\parallel$	$\chi_\parallel/\chi_\perp$
1	0	6·25	−0·307	−0·296	−0·329	1·11
2	0·43	6·23	−0·285	−0·280	−0·295	1·06
3	0·67	6·27	−0·273	−0·270	−0·279	1·03
4	1·06	6·35	−0·254	−0·252	−0·258	1·02

The influence of lead is definitely to lower the susceptibility values and the anisotropy.

Tin.—Tin is of great interest since it is paramagnetic while tellurium is diamagnetic. The specific susceptibility of the tin used was found by the Curie method to be $+0·038$ which agrees with standard measurements.

Hart[6] found that the effect of adding small quantities of tin to antimony is to lower the magnetic anisotropy of antimony. While $\chi_\perp$ is unaffected, $\chi_\parallel$ decreases gradually on the addition of tin. The results obtained here with tellurium alloyed with small quantities of tin are presented in Table X.

TABLE X

Specimen No.	% by weight of tin	Density gm./c.c.	Mean χ	$\chi_\perp$	$\chi_\parallel$	$\chi_\parallel/\chi_\perp$
1	0	6·25	−0·307	−0·296	−0·329	1·11
2	0·62	6·17	−0·303	−0·295	−0·319	1·05
3	0·95	6·09	−0·298	−0·295	−0·304	1·03
4	1·20	6·01	−0·290	−0·288	−0·294	1·02

$\chi_\perp$ decreases very slightly but $\chi_\parallel$ decreases more rapidly. The magnetic anisotropy decreases to unity.

Bismuth.—The sample of bismuth used was found to have a susceptibility of $-1·345$ which agrees very well with the values obtained by other investigators. The results are given in Table XI.

TABLE XI

Specimen No.	% by weight of bismuth	Density gm./c.c.	Mean χ	$\chi_\perp$	$\chi_\parallel$	$\chi_\parallel/\chi_\perp$
1	0	6·25	−0·307	−0·296	−0·329	1·11
2	0·38	6·20	−0·292	−0·284	−0·308	1·08
3	0·93	6·21	−0·274	−0·270	−0·282	1·03

All the susceptibility values decrease rapidly.

The order of decrease is similar to what is observed with lead.

Cadmium.—The specific susceptibility of the cadmium used was found to be −0·175. Tellurium has six valence electrons. Lead and tin have only four valence electrons; bismuth has five while cadmium has only two. We are thus enabled to find out the influence of the number of valence electrons in the added metal on the susceptibility of tellurium. The results are shown in Table XII.

TABLE XII

Specimen No.	% by weight of cadmium	Density gm./c.c.	Mean χ	$\chi_\perp$	$\chi_\parallel$	$\chi_\parallel/\chi_\perp$
1	0	6·25	−0·307	−0·296	−0·329	1·11
2	0·52	6·18	−0·298	−0·290	−0·314	1·08
3	0·88	6·13	−0·290	−0·286	−0·298	1·04

The susceptibilities of the metal decrease when the concentration of cadmium is increased. The anisotropy also shows a decrease.

General Conclusions.—The effects of adding small quantities of foreign metals on the susceptibility of tellurium are generally similar in the case of all the metals added. All the elements added produce a decrease in the principal susceptibilities, the susceptibility of the polycrystalline form and the magnetic anisotropy of tellurium.

The changes which take place when foreign metals are added to tellurium are also similar to the susceptibility changes when tellurium is heated.

Fig. 4 shows the variation of the mean susceptibility of tellurium when small quantities of tin, cadmium, bismuth and lead are added. The concentration of the foreign metal is expressed in atomic per cent. and plotted along the X-axis. It is found that lead produces the largest deviation. The deviation is least in the case of tin. Cadmium which possesses two valence electrons produces a larger deviation than tin, which possesses four valence electrons. Similarly lead which has only four valence electrons produces a larger deviation than bismuth which has five valence electrons per atom. These results show that the deviations are not dependent on the number of valence electrons in the atom of the metal added to tellurium.

5. *Discussion*

We now proceed to calculate the atomic susceptibilities parallel and perpendicular to the trigonal axis. These are respectively $-42{\cdot}0$ and $-37{\cdot}8$. The susceptibility of a gram ion (Te^{+6}) of tellurium is found by Kido[14] to be $-4{\cdot}5$. The susceptibility of the metal is hence due almost entirely to the susceptibility of the six valence electrons. Since the atomic susceptibility of polycrystalline tellurium works to $-39{\cdot}2$ the contribution to the atomic susceptibility made by the six valence electrons is $-34{\cdot}7$ being diamagnetic. This will happen only if all the six valence electrons (or most of them) have no metallic linkages.

The free or loosely bound electrons in one gram atom of a metal contribute a paramagnetic susceptibility given by[22]

$$(\chi_A)_e \times 10^6 = 32{\cdot}11\left(\frac{q}{V_0}\right),$$

where q is the number of valence electrons per atom and V_0 is the width in volts of the occupied energy range of the electrons in the completely degenerate state. It is clear that the valence electrons in tellurium do not contribute any such paramagnetic component.

That the linkages of the valence electrons in tellurium are not metallic is also shown by the fact that the application of Landau's equation[23] for diamagnetism

$$\chi_L = -0{\cdot}623 n_0^{\frac{1}{3}}\ \rho^{-\frac{2}{3}}\ A^{-\frac{1}{3}} \times 10^{-6}$$

(where ρ is the density, A the atomic weight and n_0 the number of free electrons per atom), does not yield for the mass susceptibility of tellurium a value which agrees with either the solid or liquid value for tellurium. A calculation gives for χ_L the value $-0{\cdot}066$ and hence the resultant mass susceptibility of the electrons if they are free, is $+0{\cdot}132$. The ionic susceptibility per gram of tellurium is $-4{\cdot}5/127{\cdot}6$ or $-0{\cdot}035$. Hence the mass susceptibility of tellurium works to $+0{\cdot}098$. The mass

susceptibility of tellurium is $-0{\cdot}309$ in the solid state and $-0{\cdot}046$[11] in the liquid state.

These considerations lead us to infer that from the magnetic point of view tellurium behaves like a non-metal although in several physical properties it resembles a metal. Bridgman[24] gave for the specific resistance of tellurium crystals at 20° C. the values of 5,600 ohms when parallel and 15,400 ohms when normal to the chief axis. The specific resistance of the metal is therefore very large. In this behaviour it is different from ordinary metals. What is of further interest is that the resistance is different along and normal to the trigonal axis. The thermal conductivity of tellurium perpendicular to the principal axis, is $0{\cdot}65$ times the conductivity along the principal axis. Bridgman[25] gave for the linear thermal expansion at 20° C., $-1{\cdot}6 \times 10^{-6}$ when parallel and $27{\cdot}2 \times 10^{-6}$ when perpendicular to the trigonal axis. This means that the crystal contracts along the trigonal axis when heated. In this investigation it is shown that magnetic susceptibility is also different along and normal to the trigonal axis.

If the valence electrons of tellurium contribute almost completely to the diamagnetic susceptibility of the metal, it is likely that they have a homopolar binding. The valence electrons of Te atom are the two $5s$ electrons and four $5p$ electrons. It looks probable that the $5s$ electrons are shared by two neighbouring atoms in the spiral of the tellurium crystal and that the four $5p$ electrons are shared by the atoms in adjacent lattices. When foreign atoms are introduced, it is likely that they occupy the vacant spaces between the lattice planes. They will then affect the susceptibility contribution of the four $5p$ electrons and the diamagnetic susceptibility shows a decrease in value.

This point of view appears to gain some weight from considerations of the sizes of the introduced atoms.

TABLE XIII

Atom	Radius in Å units
Te	1·439
Pb	1·747
Sn (White) ..	1·400
Bi	1·556
Cd	1·486

Table XIII gives the atomic radii of the elements taken from Clark's *Applied X-Rays* (pp. 234–44). It is interesting to observe in Fig. 4 that the magnitude of the change of susceptibility of tellurium produced by the addition of foreign metals is dependent on the radius of the atom of the foreign metal. Lead which has the largest atomic radius produces the largest decrease of susceptibility. As we proceed from lead to bismuth, cadmium and tin, the atomic radius decreases. There is also a corresponding decrease in the value of the diamagnetic susceptibility of the tellurium alloy as presented in Fig. 4.

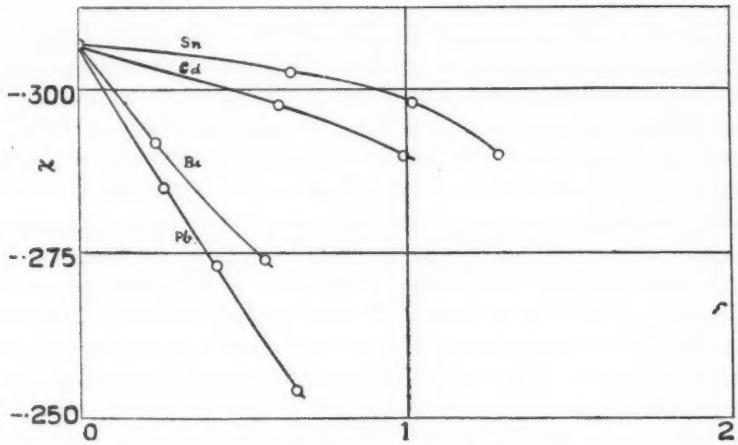

FIG. 4

It may be shown by simple calculation that the decrease of the diamagnetic susceptibility of tellurium, produced by the introduction of foreign atoms, is much larger than what is given by the law of additivity.

It may therefore be taken as definitely established that foreign atoms decrease the diamagnetic susceptibility of tellurium to a considerable extent. This decrease is dependent only on the size of the introduced atom and not on the number of valence electrons this atom carries.

6. *Summary*

The principal diamagnetic susceptibilities of tellurium crystal have been determined. The principal susceptibilities are found to be $-0{\cdot}329$ parallel to the trigonal axis and $-0{\cdot}296$ perpendicular to the trigonal axis. This leads to a value of $1{\cdot}11$ for the magnetic anisotropy of the

crystal. The susceptibility of well-annealed polycrystalline tellurium is found to be $-0{\cdot}307$. This value agrees favourably with those of other investigators.

When heated, the susceptibility parallel to the trigonal axis decreases, while the other principal susceptibility remains constant. At 220° C., the two susceptibilities become equal. When the solid melts, the volume susceptibility decreases from $-1{\cdot}7$ to $-0{\cdot}3$.

A study has also been made of the principal diamagnetic susceptibilities of tellurium containing small admixtures of tin, cadmium, bismuth and lead. In all these cases, both the principal diamagnetic susceptibilities show a decrease in value and the magnetic anisotropy tends to unity. The diamagnetic susceptibility of the polycrystalline tellurium also suffers a decrease. This decrease is found to be larger, the greater the atomic radius of the element introduced. The number of valence electrons in the atom of the added element does not seem to have any influence on the decrease in the susceptibility of tellurium.

The atomic susceptibility of polycrystalline tellurium is found to be $-39{\cdot}2$ while according to Kido the susceptibility of a gram ion of tellurium (Te^{+6}) is $-4{\cdot}5$. The contribution to the total atomic susceptibility of the element by the six valence electrons is $-34{\cdot}7$. This indicates that the linkages of all the six electrons are not metallic. Tellurium, therefore, behaves like a non-metal. This conclusion is substantiated by the large electrical resistance of the element. Attention is also drawn to the difference in the values of electrical and thermal conductivities and linear expansion coefficients along and normal to the trigonal axis.

REFERENCES

1. *Proc. Roy. Soc.*, 1928, **9**, 121 ; *Roy. Soc. Canada Trans.*, 1929, **23**, 159.
2. *Phys. Rev.*, 1930, **36**, 319.
3. *Ibid.*, 1934, **45**, 170.
4. *Ann. der Phys.*, 1934, **21**, 791.
5. *Phys. Rev.*, 1935, **48**, 615.
6. *Ibid.*, 1937, **52**, 130.
7. *Proc. Roy. Soc.*, 1936, **158**, 687 & 701.
8. *Ibid.*, 1938, **166**, 325.
9. *Phil. Mag.*, 1936, **21**, 609.
10. *Ibid.*, 1938, **26**, 1018.
11. *Ann. der Phys.*, 1910, **32**, 1027.
12. *Sc. Rep. Tohoku Imp. Univ.*, 1933, **22**, 835.
13. *Mellor's Treatise*, 1931, **11**, 20.

14. *Phys. Rev.*, 1923, **21**, 378.
15. *Phil. Mag.*, 1924, **58**, 477.
16. *Applied X-Rays*, 1932, p. 243.
17. *Proc. Ind. Acad. Sci.*, (A), 1936, **4**, 186.
18. *Mellor's Treatise*, 1931, **11**, 22.
19. *Roy. Soc. Canada Trans.*, 1929, **23**, 159.
20. *Comp. Rend.*, 1911, 117.
21. *Phil. Mag.*, 1928, **5**, 36.
22. Stoner, *Magnetism and Matter*, 1934, p. 504.
23. Mott and Jones, *Properties of Metals and Alloys*, 1936, p. 210.
24. *Mellor's Treatise*, 1931, **11**, 18.
25. *Ibid.*, 1931, **11**, 15.

A STUDY OF THE CONTINUOUS WINGS OCCURRING IN RAMAN EFFECT

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(Communicated by Prof. S. Bhagavantam)

1. Introduction

Some results relating to the phenomenon of continuous wings occurring in Raman effect have been published by the author in two of his earlier communications.[1,2] This paper is to be regarded as a continuation of the same.

2. Liquids Possessing Different Optical Anisotropies

The theory of rotational Raman scattering in gases shows that a direct and simple relationship should be expected to exist between the intensity of this type of scattering and the optical anisotropy of the molecule. With a view to throw some light on this question in liquids, this investigation is undertaken. Two typical liquids, namely benzene and cyclohexane, are chosen for this purpose. It may be noted here that they are both non-polar and possess widely different optical anisotropies. The times of exposure are adjusted by trial such that the peak intensity of λ 4358 remains the same in the two liquids. The two pictures are recorded on the same plate and the accompanying wings are microphotometered in such a way that one is superposed on the other, as illustrated in Fig. 1. The more intense curve corresponds to the wing obtained with benzene and the less intense one relates to the wing obtained in cyclohexane.* *The very large intensity exhibited by the wing in benzene in comparison with that found in cyclohexane is an outstanding feature of Fig.* 1.

The same procedure as above is repeated with the same pair of liquids, but after interposing a suitably orientated Nicol in the path of the scattered light such that only the horizontal components are recorded. The wings are microphotometered, such that the curves are superposed on one another

* Intensity here refers to the intrinsic intensity of the wing and not to be understood as drawing a distinction between the intensities with which the two curves are printed.

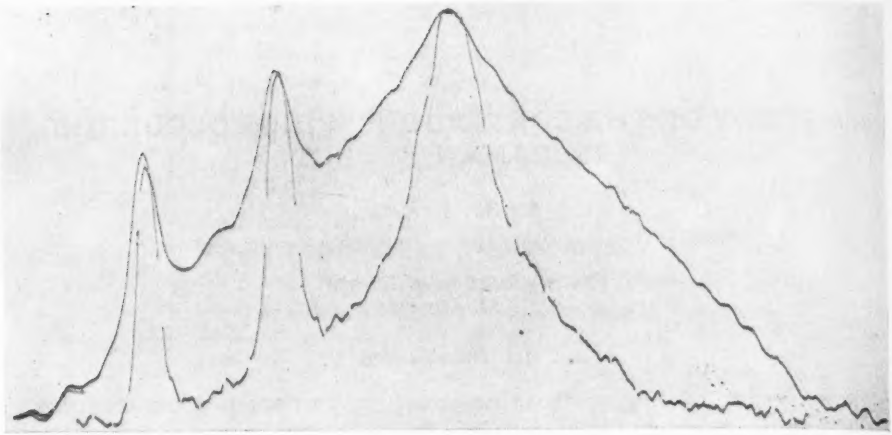

FIG. 1

Benzene and Cyclohexane

(Fig. 2). The more intense curve corresponds to benzene and the less intense one to cyclohexane. Even when the *horizontal components alone are compared, it is clear that the wing in benzene is more intense than that*

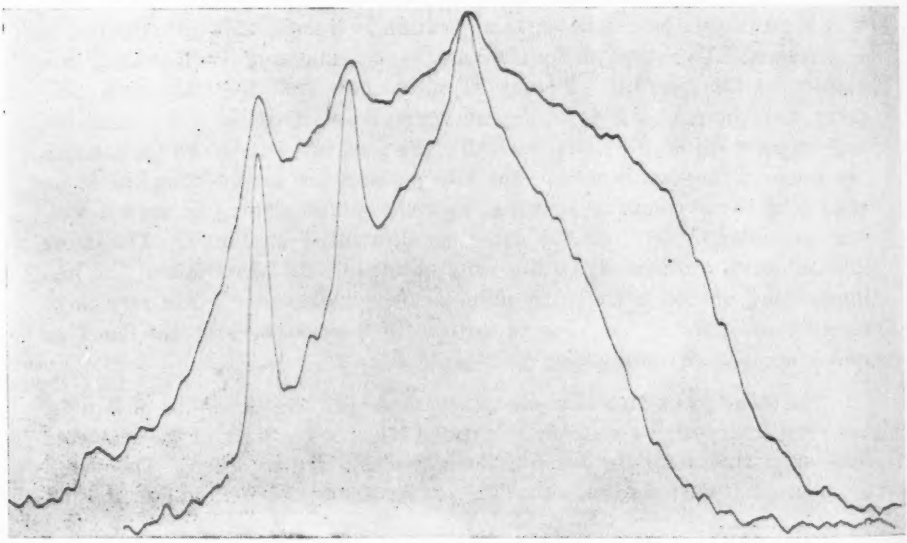

FIG. 2

Benzene and Cyclohexane, horizontal components only

obtained in cyclohexane. This is so in spite of the fact that these two molecules have similar structures and possess nearly the same moments of inertia.

Another pair of liquids, namely cyclohexane and acetic acid, are studied in a similar manner. In Fig. 3 the more intense curve corresponds to cyclohexane and the less intense one refers to acetic acid. *It is interesting to note that though the optical anisotropy of cyclohexane is less than that of acetic acid, the horizontal component of the wing in cyclohexane is definitely more intense than that obtained in acetic acid.*

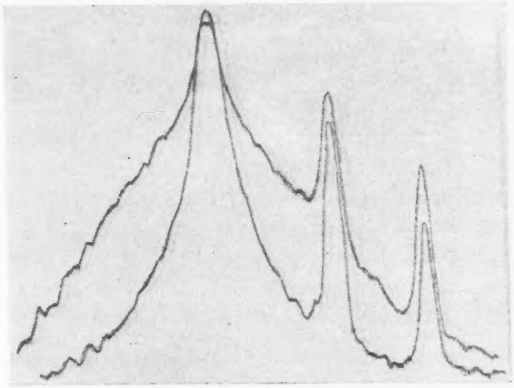

FIG. 3

Cyclohexane and Acetic Acid, horizontal components only

3. *Liquids possessing the Same Optical Anisotropy*

Acetic acid and benzene are two typical examples of a pair of liquids, exhibiting the same depolarisation factor and possessing nearly the same optical anisotropy. The wings obtained in these cases are similarly compared with each other by keeping the peak intensity the same in both. In this case, a nicol is not interposed and the results refer to total scattering. The figure is not reproduced in this paper as it is similar to those already given. We conclude that *acetic acid which is a highly associated liquid exhibits a wing which is much less intense than that obtained in benzene although both the susbstances are optically anisotropic to more or less the same extent.* The above results readily enable us to see that no simple relation between the optical anisotropy and the intensity of this type of scattering exists in the case of liquids. Similar results have been obtained earlier by Veerabhadra Rao[3] working with benzene and formic acid. Raman and Venkateswaran[4] have recently worked with benzene, acetic acid, salol and glycerine and have shown that this type of scattering becomes less and less marked

as we go along the series until it becomes practically negligible in glycerine. They have connected this fact with the increased viscosity of glycerine and concluded that the highly viscous liquids are to be treated as akin to amorphous solids for purposes of light scattering.

4. *An Attempt to Detect the Maximum in the Liquid Wing at High Temperatures*

Although several investigators have reported that they could not find any maximum within the wing which is well separated from the centre in liquids, Sirkar and Maiti[5] claimed to have obtained different results in liquid benzene. These authors made use of a Fuess glass spectrograph and after making a correction for the broadening of the Rayleigh line, obtained results similar to those in gases. Subsequently Bhagavantam[6] worked on the same problem, using a Hilger high dispersion instrument and found that no such maximum could be obtained with benzene. His results are in agreement with those of all the other earlier workers. The author has nevertheless repeated the work again, and his results which confirm this conclusion are not reproduced here as it is considered unnecessary. *It may therefore be taken that the absence of a separated maximum in the liquid wing at the room temperature is now well established.*

Sirkar and Maiti also claimed to have obtained a separated maximum at the expected place at the high temperatures. As Bhagavantam's investigations refer only to the room temperature, the claim of Sirkar and Maiti relating to the high temperature remains unconfirmed. It is therefore thought necessary to extend the quantitative investigations on the intensity distribution to high temperatures under suitable experimental conditions. A high dispersion instrument (Hilger, Littrow E 349) is specially chosen for this purpose and the wings accompanying λ 4358 are recorded after raising the benzene tube to 200° C. A thick wall sealed tube and a suitable

TABLE I

Intensity Distribution in the Wing of Benzene at 200° C.

$\Delta\nu$ cm.$^{-1}$	5·5	11	16·5	22	27·5	33	33·5	44	49·5	55
(Author) Intensity 200° C.	3631	2754	1905	1585	1096	831·8	691·8	575·4	436·5	363·1
(A. V. Rao) Intensity 30° C.	..	2754	1542	991·3	..	638·9	..	453·7	..	356·9

electric furnace have been used for this purpose. Intensity marks are given on the same plate by the method of varying slit-widths. The intensity distribution for the wing accompanying λ 4358 is calculated and the results are given in Table I.

Veerabhadra Rao's[7] results obtained at the room temperature are increased proportionately to facilitate graphical representation and given in Table I for comparison. These results are graphically represented in Fig. 4. The curve showing the intensity distribution within the wing at the high temperature has been carried into regions so close as 10 wave numbers, but no separated maximum has been detected. According to the contention of Sirkar and Maiti, as well as the expectations from the theory applicable to gases, the maximum is expected to be present at about 22 cm.$^{-1}$ from the centre. The high dispersion of the instrument employed can easily show this position distinctly separate from the centre, if it is present. The fine slit employed and the high optical quality of the

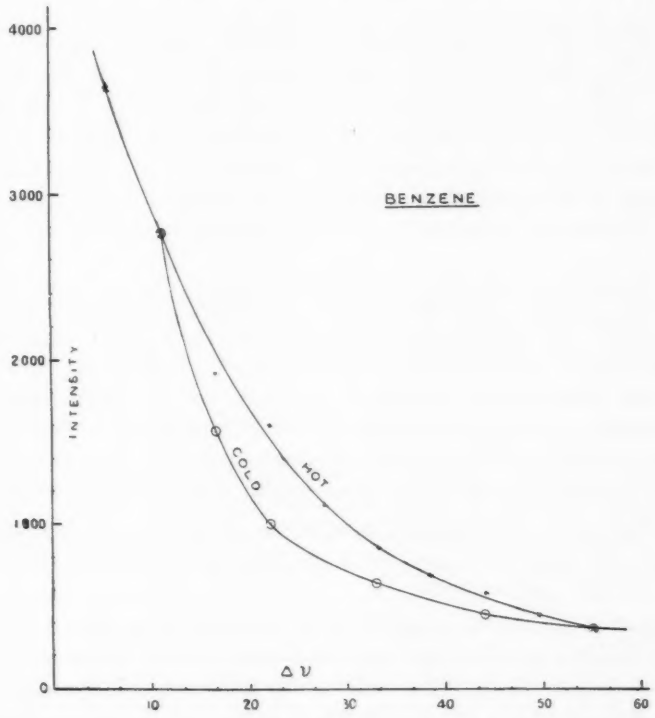

FIG. 4

instrument enable us to dispense with the correction for the broadening of the centre altogether. We may accordingly conclude that *even at high temperatures such as 200°C. there is no maximum well separated from the centre in the wing accompanying the Rayleigh lines in liquid benzene.*

It may however be noted that Fig. 4 shows *an increase in the intensity of the central portion of the wing in conformity with the observations recorded in the earlier papers.*

5. Discussion of Results

The main conclusions that have been arrived at either for the first time in the present investigation or confirmed by repeating the work of the earlier authors have been given in italics within the foregoing sections. These are collected below for purposes of convenience of discussion.

1. The very large intensity exhibited by the wing in benzene in comparison with that found in cyclohexane is an outstanding feature of Fig. 1.

2. Even when the horizontal components alone are compared, it is clear that the wing in benzene is more intense than that obtained in cyclohexane. This is so in spite of the fact that these two molecules have similar structures and possess nearly the same moment of inertia.

3. It is interesting to note that though the optical anisotropy of cyclohexane is less than that of acetic acid, horizontal component of the wing in cyclohexane is definitely more intense than that obtained in acetic acid.

4. Acetic acid which is a highly associated liquid exhibits a wing which is much less intense than that obtained in benzene, although both the substances are optically anisotropic to more or less the same extent.

5. The absence of a separated maximum in the liquid wing at the room temperature may now be regarded as well established. Even at high temperatures such as 200° C. there is no maximum well separated from the centre in the wing accompanying the Rayleigh lines in liquid benzene.

6. There is an increase in the intensity of the central portion of the wing when the temperature is raised in conformity with the observations recorded in the earlier papers.

In order to discuss the significance of the facts collected here, we have to briefly mention some of the more important results obtained in other branches of Raman effect. It is well known that inorganic crystals such as calcite or sodium nitrate exhibit discrete Raman lines in the neighbourhood

of the Rayleigh line. Organic crystals such as naphthalene, solidified benzene, etc., have also been found to exhibit similar Raman lines. Occasional attempts have been made in the literature to explain the origin of such low frequency Raman lines and some authors have suggested that their origin is not the same in the organic substances as that in the inorganic crystals. This is a very important point and it has been recently stressed by Bhagavantam and Venkatarayudu,[8] that they have to be considered as lattice oscillations in both the cases and that there is no essential difference between the organic and inorganic solids in this respect. By a detailed analysis in some typical cases they have shown, that these lattice lines have to be attributed to either translatory or rotatory movements of the molecules or ions which go to build up the crystal. On account of the fact that the molecules or ions are bound to their equilibrium positions by crystalline forces, the above movements are only incomplete and have necessarily to take place on either side of the equilibrium position, the amplitude being limited by the energy of the motion.

Organic liquids have been known to exhibit continuous wings in this region. It is only recently that Nedungadi[9] and Moses[10] have shown that fused inorganic crystals as well exhibit very similar wings in these regions. The work of the latter author has been of particular help in revealing the close similarity that exists between the wings that are obtained in organic liquids on the one hand and fused inorganic salts on the other. In this respect also no distinction need therefore be drawn between the inorganic and the organic substances.

In the case of vapours, extensive work has not been done, but several gases have been studied. The meagre results available in the case of vapours taken together with the results that are available in gases, enable us to conclude that the spectra recorded in the neighbourhood of the Rayleigh line are due in both the cases, to the rotational Raman effect caused by molecules freely rotating subject to the usual laws of kinetic theory.

We have accordingly to look at these phenomena, namely discrete lines in the case of solids, continuous wings in the case of liquids, and rotational Raman effect in the case of gases—all of which occur in the neighbourhood of the Rayleigh line as one comprehensive unit. In interpreting them, their observed characters have to be taken into account. There is very little doubt regarding their origin in solids and in gases, since they are two extreme cases. The difficulty however arises in the case of liquids only, but if we look at the transition solid-liquid-gas, as a process by which the thermal movements of the molecules become more vigorous, it is obvious

that the sharply quantised rotatory or oscillatory motions that are known to occur in solids, have to pass through a stage in which their amplitudes are rather large and quantisation somewhat imperfect, before we reach the case of complete rotations and free translations that occur in gases. It is suggested here, that the intermediate stage is what exists in a liquid. In other words, we postulate that the same type of oscillations (lattice) that occur in a regular crystal, also occur in a liquid but in a more disorderly manner, giving rise to continuous wings. These have been termed the hindered rotations in earlier papers.

Such a view is in satisfactory agreement with the experimental facts obtained by the author. The increase in the central portion of the wing stands explained, since an increase in temperature should be expected to result in an increased amplitude of the motion. The simple relationship between the optical anisotropy and the intensity of the low frequency Raman scattering should be expected to break down in liquids. The additional part played by dipole association, viscosity, etc., which results in increased internal fields in a liquid, thus hampering the movements of the molecules is easily understood. That a well separated maximum at the expected place has not been recorded even at a temperature of 200 °C., in liquid benzene, should be taken as evidence in favour of the view that the molecules are not yet free to rotate as in a gas.

6. *Summary*

Certain features characteristic of the continuous wings occurring in the Raman spectra of liquids are studied. It is concluded that besides the optical anisotropy, other physical properties of the liquid such as its viscosity and dipole association play a prominent part in determining the intensity of these wings. No separated maximum could be detected in the wing obtained with liquid benzene even at a temperature of 200° C. The results are discussed in the light of the existing literature.

The author wishes to express his grateful thanks to Prof. S. Bhagavantam, for his kind interest and valuable guidance during the course of this investigation.

REFERENCES

1. Bapayya .. *Curr. Sci.*, 1937, **5**, 532.
2. ———— .. *Proc. Ind. Acad. Sci.*, 1939, **9**, 404.
3. Rao .. *Thesis* submitted to the Andhra University, 1935.
4. Raman and Venkateswaran *Nature*, 1939, **143**, 798.
5. Sirkar and Maiti .. *Ind. Jour. Phys.*, 1934, **9**, 323.
6. Bhagavantam .. *Proc. Ind. Acad. Sci.*, 1935, **2**, 342.
7. Rao .. *Ibid.*, 1934, **1**, 274.
8. Bhagavantam and Venkatarayudu *Ibid.*, 1939, **9**, 224.
9. Nedungadi .. *Ibid.*, 1938, **8**, 397.
10. Moses .. *Ibid.*, 1939, **10**, 71.

HETEROCYCLIC COMPOUNDS

Part X. The Synthesis of Substituted 1 : 2 : 3 : 4 -Tetrahydroacridones

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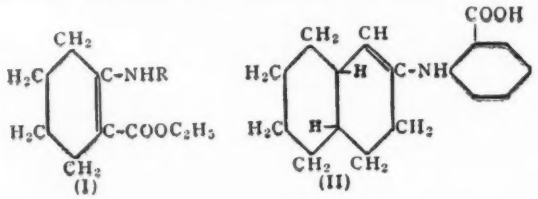
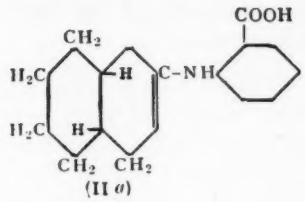
As stated in Part II of this series,[1] we are busy studying the condensation of aromatic amines with cyclic β-Ketonic esters under varying conditions, with the object of preparing 2-hydroxy- and 4-hydroxy-quinoline derivatives. Owing to unforeseen circumstances, our work has not reached a complete stage, but it has been deemed necessary to publish some of our results with cyclohexanone-2-carboxylate because of the recent publication of Hughes and Lions.[2]

Ethyl-cyclohexanone-2-carboxylate was condensed with, *o*-toluidine, *p*-bromaniline, *o*-anisidine, *p*-anisidine and *p*-phenetidine according to the method of Coffey, Thompson and Wilson[3] with the formation of the corresponding aryaminocrotonic esters (I, where R = *o*-tolyl, *p*-bromphenyl, etc., etc.), which cyclised to their respective 1 : 2 : 3 : 4-tetrahydro-acridone derivatives on heating at 240–50°. Tetrahydroacridones have been prepared by Blount, Perkin and Plant[4] from aniline and by Sen and Basu[5] from aniline, *p*-toluidine, and *m*-xylidine by this method.

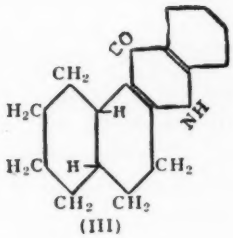
In view of the accessibility of the cyclic ketones, the alternative method of Borsche and Tiedke[6] for preparing 1 : 2 : 3 : 4-tetrahydro-acridones by condensing ketones with anthranilic acid was extended to 2-methylcyclohexanone, 4-methylcyclohexanone, and *trans*-β-decalone.

The anil obtained from *trans*-β-decalone may have the alternative structure 2-(*o*-Carboxyanilino)-$\Delta^{1:2}$-octaline (II) or 2-(*o*-carboxy-anilino)-$\Delta^{2:3}$-octaline (II *a*); consequently, the resulting octahydro, naphthacridone will be either angular (III) or linear (III *a*) in structure.

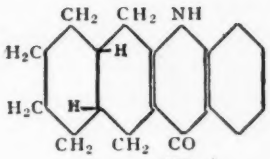




(II *a*)



(III)



(III *a*)

We are busy studying this reaction with other cyclic β-ketonic esters, and the examination of their various chemical properties.

Experimental

Ethyl 2-p-*bromanilino*-$\Delta^{1:2}$-*cyclohexene*-1-*carboxylate* (*I, where* R = *p-bromphenyl*).—A mixture of *p*-bromaniline (4 g.), ethyl cyclohexanone-2-carboxylate (4 g.) and concentrated hydrochloric acid (0·1 c.c.) was kept for 48 hours in a vacuum desiccator. The semi-solid mass was washed with hexane, and finally crystallised from benzene-petrol mixture when thick plates, m.p. 77–78°, were obtained. The substance was insoluble in dilute alkalis but soluble in dilute mineral acids on warming. Its alcoholic solution did not give any colouration with ferric chloride (yield, 5·5 g.). (Found : Br, 24·9 ; $C_{15}H_{18}O_2$ NBr requires Br, 24·7 per cent.)

7-*Bromo*-1 : 2 : 3 : 4-*tetrahydroacridone*.—The above solid was heated in an oil-bath at 240–50° for 15 minutes and cooled. The resulting solid crystallised from alcohol in small needles which did not melt upto 350°. (Found : Br, 28·5 ; $C_{13}H_{12}ONBr$ requires Br, 28·8 per cent.) It was soluble in hot dilute mineral acids, hot dilute alkali, but insoluble in sodium carbonate solution.

Ethyl 2-o-*anisidino*-$\Delta^{1:2}$-*cyclohexene*-1-*carboxylate* similarly obtained from *o*-anisidine (2·5 g.), crystallised from hexane in needles, m.p. 79–80° (yield 3 gm.). It was soluble in dilute mineral acids, alcohol, benzene, etc., but insoluble in dilute alkali. Its alcoholic solution did not give any

colouration with ferric chloride. (Found : C, 69·5 ; H, 7·7 ; $C_{16}H_{21}O_3N$ requires C, 69·8 ; H, 7·6 per cent.)

5-*Methoxy*-1 : 2 : 3 : 4-*tetrahydroacrdone*—similarly obtained from the above ester crystallised from alcohol in short needles, m.p. 277–79°. It was soluble in warm dilute mineral acids, hot dilute alkali, alcohal, acetone, etc., but sparingly soluble in benzene, and almost insoluble in hexane and petrol. (Found : C, 73·3 ; H, 6·7 ; $C_{14}H_{15}O_2N$ requires C, 73·4 ; H, 6·6 per cent.)

Ethyl 2-p-*anisidino*-$\Delta^{1:2}$-*cyclohexene*-2-*carboxylate*—similarly obtained from *p*-anisidine (2·5 g.) crystallised from hexane in needles, m.p. 71–72° (yield 3·5 g.). It was soluble in dilute mineral acids, but insoluble in alkali. Its alcoholic solution did not give any colouration with ferric chloride. (Found : C, 69·6 ; H, 7·8 ; $C_{16}H_{21}O_3N$ requires C, 69·8 ; H, 7·6 per cent.)

7-*Methoxy*-1 : 2 : 3 : 4-*tetrahydroacridone*—obtained by the usual method crystallised from alcohol in short needles, m.p. 285–86.° It was soluble in warm, dilute mineral acids, hot dilute alkali, alcohol, acetone, acetic acids, sparingly soluble in benzene and almost insoluble in hexane and petrol. (Found : C, 73·1 ; H, 6·6 ; $C_{14}H_{15}O_2N$ requires C, 73·4 ; H. 6·6 per cent.)

Ethyl 2-o-*toluidino*-$\Delta^{1:2}$-*cyclohexene*-1-*carboxylate*—similarly obtained from *o*-toluidine (3 g.) crystallised from hexane in thick plates, m.p. 84–85°, and had the usual properties of its analogues. (Found : C, 73·8 ; H, 8·2 ; $C_{16}H_{21}O_2N$ requires C, 74·1 ; H, 8·1 per cent.)

5-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacridone*—obtained as usual crystallised from alcohol in microscopic plates, m.p. 355–58°, and had the usual properties of its other analogues. (Found : C, 78·7 ; H, 7·2 ; $C_{14}H_{15}ON$ requires C, 78·9 ; H, 7·0 per cent.)

Ethyl p-*phenetidino*-$\Delta^{1:2}$-*cyclohexene*-1-*carboxylate*, prepared as usual from *p*-phenetidine, crystallised from hexane in prismatic needles, m.p. 88°. It was soluble in the usual organic solvents, and in dilute mineral acids. Its alcoholic solution did not give any colouration with ferric chloride. (Found : C, 70·5 ; H, 8·1 ; $C_{17}H_2O_3N$ requires C, 70·6 ; H, 8·0 per cent.)

7-*Ethoxy*-1 : 2 : 3 : 4-*tetrahydroacridone*—obtained by the usual method, crystallised from alcohol in small plates which did not melt upto 350°. It was readily soluble in warm dilute acids and alkali. (Found : C, 74·2 ; H, 7·3 ; $C_{15}H_{17}O_2N$ requires C, 74·1 ; H, 7·0 per cent.)

1-o-*Carboxy-anilino-6-methyl-*$\Delta^{1:2}$*-cyclohexene.*—A mixture of 2-methylcyclohexanone (5 g.) and anthranilic acid (5 g.) was heated in an oil-bath at 120° for nearly three hours. The mixture which solidified on cooling was washed with a little benzene, and the residue crystallised from the same solvent when tiny prisms melting at 130° were obtained. It was soluble in alcohol, acetic acid, acetone, and sodium bicarbonate solution (yield 5·5 g.). (Found : C, 72·5 ; H, 7·5 ; $C_{14}H_{17}O_2N$ requires C, 72·7 ; H, 7·4 per cent.)

4-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacridone*—obtained by heating the above anil at 220° for two hours was purfied by washing with sodium bicarbonate solution, and crystallised from benzene when tiny plates, melting at 345°, were obtained. It was soluble in hot dilute mineral acids and alkali. (Found : C, 78·8 ; H, 7·3 ; $C_{14}H_{15}ON$ requires C, 78·9 ; H, 7·0 per cent.)

1-o-*Carboxy-anilino-4-methyl-*$\Delta^{1:2}$*-cyclohexene*—similarly obtained from 4-methylcyclohexanone (5 g.) and anthranilic acid (5 g.) crystallised from alcohol in small plates, m.p. 143°. Its mixed m.p. with 1-*o-carboxyanilino-5-methyl-*$\Delta^{1:2}$*-cyclohexene*, m.p. 141°, which was prepared by Perkin and Sidgwick[7] was 110–15°. It was soluble in alcohol, acetic acid, benzene, acetone and sodium bicarbonate solution (yield 6·0 g.). (Found : C, 72·6 ; H, 7·4 ; $C_{14}H_{17}O_2N$ requires C, 72·7 ; H, 7·4 per cent.)

3-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacridone*—obtained by the usual method, crystallised from benzene in small plates which did not melt up to 350°. (Found : C, 78·7 ; H, 7·1 ; $C_{14}H_{15}ON$ requires C, 78·9 ; 7·0 per cent.)

2-o-*Carboxyanilino-*$\Delta^{(1:2)\ or\ (2:3)}$*-trans-octaline*—similarly obtained from *trans*-β-decalone (7 g.) and anthranilic acid (6 gm.) crystallised from benzene in microcrystalline plates melting at 164–65°. The monohydrate is obtained when this product crystallises from dilute alcohol in thick rhomboids, m.p. 82°. It reverts to the anhydrous form, m.p. 164–65°, after being dried at 110°. The anhydrous form was used for the analysis. (Found : C, 75·1 ; H, 7·7 ; $C_{17}H_{21}O_2N$ requires C, 75·3 ; H, 7·7 per cent.) (Found loss in weight = 6·41 ; $C_{17}H_{21}O_2N.\ H_2O$ requires loss in weight = 6·2 per cent.)

The substance was soluble in alcohol, acetic acid, acetone, benzene and sodium bicarbonate solution (yield = 7 g.).

$\Delta^{(1:2)\ or\ (2:3)}$*-Octahydronaphthacridone*—prepared from the above compound as usual crystallised from benzene in tiny prisms, which did not melt upto 350°. (Found : C, 80·3 ; H, 7·6 ; $C_{17}H_{19}ON$ requires C, 80·6 ;

H, 7·5 per cent.) It was soluble in alcohol, acetone, acetic acid and warm dilute mineral acids and alkali.

Summary

Substituted 1 : 2 : 3 : 4-tetrahydroacridones have been prepared by the cyclisation of the β-arylaminocrotonic esters obtained from ethyl cyclohexanone-2-carboxylate and *o*-toluidine, *p*-bromaniline, *o*-anisidone, *p*-anisidine and *p*-phenetidine. Borsche and Tiedke's method of preparing substituted tetrahydro-acridones has been applied to 2-methylcyclohexanone, 4-methylcyclohexanone and *trans*-β-decalone.

REFERENCES

1. Z. Ahmad and Desai .. *Proc. Ind. Acad. Soc.*, 1937, **5**, 543.
2. Hughes and J. Lions .. *Proc. Roy. Soc.*, New South Wales, 1938, **71**, 458.
3. Coffey, Thompson and Wilson *J.*, 1936, 856.
4. Blount, Perkin and Plant *Ibid.*, 1929, 1975.
5. Sen and Basu .. *Jour. Ind. Chem. Soc.*, 1930, **7**, 435.
6. Borsche and Tiedke .. *Ber.*, 1908, **41**, 2203 ; 1909, **42**, 624.
7. Perkin and Sidgwick .. *J.*, 1924, 2442.

GEOMETRICAL INVERSION IN THE ACIDS DERIVED FROM THE COUMARINS

Part VII. The Behaviour of Acetyl Coumaric Acids

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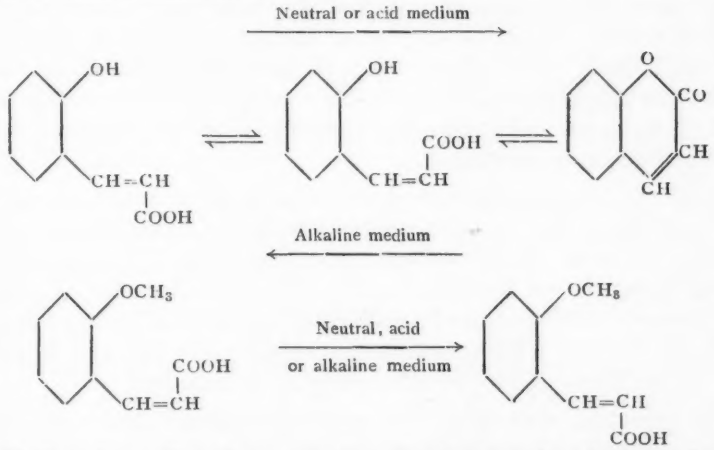
It was originally noticed by Seshadri,[1] and Seshadri and Rao[2,3] that in the case of the acids derived from the coumarins the *cis* to *trans* inversion takes place in an alkaline medium, whereas the reverse happens under neutral or acid conditions. More recently, however, Rangaswami and Seshadri[4] observed that, since normally the *trans* is the stabler form, *cis* to *trans* inversion always takes place irrespective of the nature of the medium, provided the tendency of the unstable coumarinic acids to change into the stable coumarins through ring closure is precluded by the protection of the phenolic hydroxyl group through methylation. Even here, when the chance for the hydrolysis of the methyl ether group exists as with sulphuric acid, coumarins are formed.



Methoxyl or alkoxyl groups in general are quite stable and do not undergo change except under drastic conditions. Acyl groups such as the

acetyl are, on the other hand, mild in their protective effect. The part played by such mild protective groups seems to have a bearing on the problem of the biogenesis of coumarins. In regard to the origin and occurrence of coumarins in plants, all available evidence seems to indicate that coumaric acids are the immediate precursors and they slowly undergo change under the influence of light or other causes to produce coumarins. Coumarin itself occurs in nature along with coumaric and melilotic acids and a glucoside of coumaric acid has been isolated from plant sources.

A study of the behaviour of acetyl coumaric acids has, therefore, been undertaken with a view to understand the degree of protection which mild groups can give and the facility with which these compounds can undergo change. We have now investigated the action of light, heat and mercuric chloride in neutral medium on the acetyl derivatives of the following *trans* acids :—(1) Coumaric acid, (2) 4-methylcoumaric acid, (3) 5-nitrocoumaric acid, (4) psoralic acid, and (5) isopsoralic acid. All these acids are readily obtained from the corresponding coumarins by treatment with mercuric oxide and sodium hydroxide according to the method of Seshadri and Rao.[2,5]

Acetyl coumaric acid was originally prepared by Tiemann and Herzfeld[6] as a bye-product in the preparation of coumarin from salicylaldehyde. The same acid was obtained by Stoermer[7] by the direct acetylation of coumaric acid with anhydrous sodium acetate and acetic anhydride at the boiling point of the anhydride. It has now been more conveniently produced with better yields by acetylating coumaric acid at the temperature of the steam-bath (100°). The other acids also undergo smooth acetylation by adopting this modification. If they are acetylated at the boiling temperature of the acetic anhydride, they undergo conversion considerably into the corresponding coumarins.

From the experiments on acetylation it could be concluded that the acetyl derivatives that are first produced undergo further change into the coumarins to more or less extent depending upon the conditions. At 100° the change is very small in all cases, whereas at about 150° (the temperature required for keeping acetic anhydride boiling in the reaction mixture) the conversion is very little with acetyl coumaric acid and very large with acetyl nitrocoumaric acid, the others coming in between.

The action of ultra-violet light on acetyl coumaric acid in alcohol or benzene solutions was originally studied by Stoermer (*loc. cit.*) and acetyl coumarinic acid in a considerable amount and a small quantity of coumarin were stated to have been produced.

Under the influence of sunlight which has been shown by Dey, Rao and Seshadri[8] to be an effective and convenient substitute for ultra-violet light, the acetyl coumaric acids in general undergo very slow transformation. In most cases very little change is noticed within 48 hours when alcoholic solutions are employed, and after prolonged exposure for 200 hours considerable yields of coumarins are obtained. Acetyl coumarinic acids could not be isolated amongst the products. The acetyl derivative of 5-nitrocoumaric acid is somewhat different in its behaviour. A change of about 40 per cent. is observed even within 48 hours. This difference may be due to some extent to the influence of the nitro-group in facilitating geometrical inversion. It has been already shown that nitrocoumaric acid and its methyl and ethyl esters undergo change in the presence of sunlight more vigorously than those that do not have the nitro-group. This effect of the nitro-group cannot however be the major factor because ordinary coumaric acids and their esters undergo considerable change into coumarins within 24 hours. The more important factor, therefore, seems to be the facility with which the pyrone ring closes up by eliminating a molecule of acetic acid. A nitro-group in the *para*-position obviously makes the acetoxy group more reactive and favours this change. A similar explanation holds good in regard to the behaviour of these acetyl acids under the influence of heat.

TABLE I

Acetyl derivative of	Percentage conversion under the influence of light		
	After 24 hours	After 48 hours	After 200 hours
1. Coumaric acid ..	Nil	Negligible	85 to 90%
2. 4-Methylcoumaric acid	Nil	Negligible	80 to 85%
3. 5-Nitrocoumaric acid ..	5%	40%	95 to 100%
4. Psoralic acid ..	Nil	..	..
5. Isopsoralic acid ..	Nil	..	..

When the acetyl compounds are heated to temperatures above their melting points considerable conversion into the corresponding coumarins takes place. This is, however, accompanied by the production of some resinous products also. As volatile products, along with acetic acid, some carbon dioxide is also evolved. It is therefore clear that two simultaneous reactions take place, one involving ring closure with the removal of one

molecule of acetic acid and the other involving elimination of carbon dioxide producing resinous products (see formulæ given below). In this respect the acetyl coumaric acids fall midway between coumaric acids which undergo almost completely decarboxylation on heating and the methyl and ethyl esters of coumaric acids which produce coumarins as the main product. The resinous matter obtained in the above reactions with acetyl compounds is probably produced as the result of polymerisation of the styrenes that have been formed by decarboxylation.

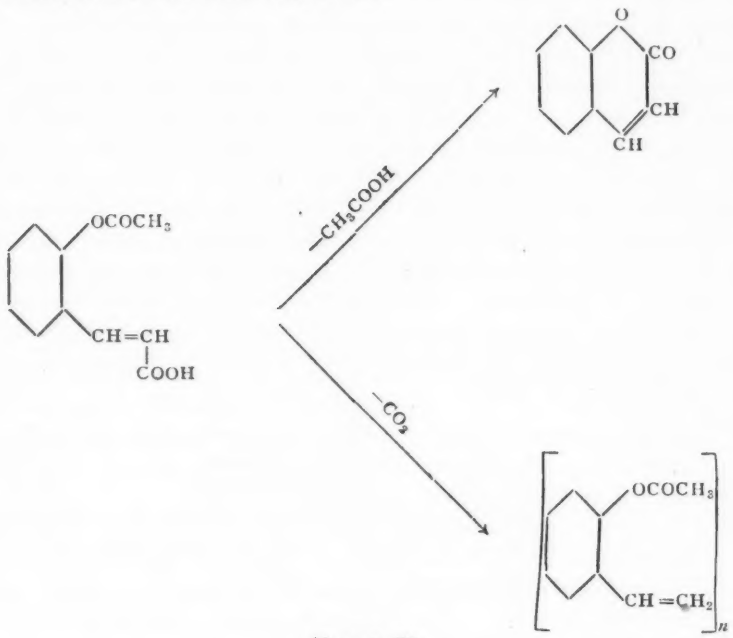


TABLE II

No.	Acetyl derivative of	Percentage conversion under the influence of heat
		%
1	Coumaric acid ..	60
2	4-Methylcoumaric acid	70
3	5-Nitrocoumaric acid ..	75
4	Psoralic acid	75
5	Isopsoralic acid ..	80

On boiling with mercuric chloride in alcoholic or aqueous solutions, the acetyl coumaric acids readily undergo complete conversion into the coumarins.

Experimental

Preparation of Acetyl Coumaric Acids—

Acetyl Coumaric Acid.—Coumaric acid (2 g.), anhydrous sodium acetate (5 g.) and acetic anhydride (20 c.c.) were heated for six hours by immersing in a boiling water-bath. The reaction mixture was then cooled and poured into 100 c.c. of ice-cold water. After leaving overnight, the acetyl derivative that separated out was purified by dissolution in aqueous sodium bicarbonate at 0° and subsequent reprecipitation from the clear filtrate with dilute hydrochloric acid. During this process the temperature should not be allowed to rise above 0° as otherwise the acetyl derivative undergoes some hydrolysis. The precipitated solid was then crystallised from benzene, when it came out as rectangular plates melting at 154–55°. (Tiemann and Herzfeld[6] gave the crystal structure as needles and the melting point as 146°; Roth and Stoermer[9] reported the melting point to be 154–55°.) The yield of the pure acetyl coumaric acid was 2·2 g. When the acetylation was carried out at a higher temperature by keeping the acetic anhydride boiling, the yield was lower (2·0 g.).

Acetyl 4-Methylcoumaric Acid.—The same procedure as in the previous case was adopted to acetylate 4-methylcoumaric acid. After purification, the substance crystallised from alcohol as fibrous needles melting at 155°. The yield was almost theoretical. (Found: C, 64·9; H, 5·0; $C_{12}H_{12}O_4$ requires C, 65·4; H, 5·4%.) The boiling temperature of acetic anhydride was not suitable for the reaction, since conversion into 7-methylcoumarin took place to a considerable extent.

Acetyl 5-Nitrocoumaric Acid.—This substance was conveniently prepared by acetylating 5-nitrocoumaric acid at 100° as in the previous cases. The crude product obtained by the treatment of the reaction mixture with water did not readily dissolve in bicarbonate solution, unless it had been well triturated first with a small quantity of the bicarbonate. Practically the whole of the solid went into solution by this treatment. It was subsequently reprecipitated and crystallised from benzene when it was obtained in the form of colourless rectangular rods, m.p. 217°. The yield of the pure product was 5·5 g. from 5 g. of nitrocoumaric acid. The substance was not easily soluble in alcohol. (Found: C, 52·3; H, 3·3; N, 5·7; $C_{11}H_9O_6N$ requires C, 52·6; H, 3·6; N, 5·6%.) At the boiling point of acetic anhydride the reaction yielded very little of the acetyl derivative, the product being mainly nitrocoumarin.

Acetyl Psoralic Acid.—Psoralic acid could be acetylated at the boiling point of the anhydride, provided the reaction mixture was gently refluxed only for 3 hours on an oil-bath at a temperature of 150°. Purification was effected as in the previous cases, and the yield was about 80%. It crystallised from alcohol as clusters of needles and rectangular prisms melting at 180–81°. The experiment was more conveniently carried out using a boiling water-bath for 6 hours and the yield was also found to be better. (Found : C, 62·9 ; H, 4·4 ; $C_{13}H_{10}O_5$ requires C, 63·4 ; H, 4·1%.)

Acetyl Isopsoralic Acid.—The procedure was just the same as in the case of the acetyl psoralic acid, and the yield was almost theoretical. It crystallised from alcohol in the form of needles melting at 210–11°. (Found : C, 63·5 ; H, 4·4 ; $C_{13}H_{10}O_5$ requires C, 63·4 ; H, 4·1%.)

Action of Sunlight on Acetyl Coumaric Acids.—Acetyl coumaric acid (1 g.) was dissolved in anhydrous ethyl alcohol (25 c.c.) contained in a quartz flask. The solution was then exposed to direct sunlight for 24 hours (8 hours a day). When the exposure was over, all the alcohol was distilled off and the product was treated with sufficient quantity of sodium bicarbonate solution. All the solid dissolved, indicating that no conversion of the acetyl coumaric acid into the pyrone had taken place. The bicarbonate slution on acidification yielded the original acid, which, after recrystallisation from benzene, melted at 154°.

The experiment was repeated increasing the period of exposure. Even after 48 hours there was very little change and no detectable amount of coumarin was formed. However exposure for 200 hours brought about almost complete conversion. The residue obtained after distilling off the alcohol did not dissolve in sodium bicarbonate solution. It was then crystallised from alcohol and was found to be identical with coumarin melting at 69°. Yield was about 90%.

Acetyl 4-methylcoumaric acid resembled closely the acetyl coumaric acid in its behaviour under the influence of light. As in the previous case, only prolonged exposure (200 hours) brought about inversion to an extent of 80 to 85%.

Acetyl 5-nitrocoumaric acid yielded 5% of 6-nitrocoumarin, even when the period of exposure was only 24 hours. It produced 40% yield of nitrocoumarin after 48 hours and underwent complete conversion (95–100%), when the exposure was for 200 hours.

Acetyl psoralic and isopsoralic acids did not produce any psoralen and isopsoralen, when exposed to sunlight for 24 hours. For want of sufficient material, their behaviour on longer exposures could not be further studied.

In all the above experiments relating to the action of light on the acetyl coumaric acids it was noticed that small quantities of amorphous sparingly soluble complex products were produced along with the coumarins. These were probably due to polymerisation which is known to take place with coumaric acids in the presence of sunlight.

Action of Heat.—Acetyl coumaric acid (1·5 g.) was taken into a clean dry test-tube and heated for half an hour in an oil-bath at a temperature 40–50° above the melting point of the acid with frequent stirring. A beautiful crystalline substance sublimed on to the cooler parts of the test-tube. Carbon dioxide was evolved during the heating and acetic acid could be distinctly smelt. After the decomposition was over, the test-tube was cooled, when the molten mass changed into an amorphous solid. The crystalline sublimate was carefully scraped off and after recrystallisation from alcohol was found to be identical with coumarin melting at 69°. The solid mass remaining in the test-tube was not soluble either in sodium carbonate, alcohol or ether. It was resinous and no definite compound could be isolated from it. The yield of coumarin was 60%.

Acetyl 4-methylcoumaric acid was heated at 210° as described above. Its behaviour was just the same as that of acetyl coumaric acid. There was 70% conversion into 7-methylcoumarin in this case. As regards acetyl 5-nitrocoumaric acid, the temperature was maintained at 255°, though 6-nitrocoumarin began to form even at a much lower temperature and the yield was 75%. Acetyl psoralic and isopsoralic acids were heated at 230° and 240° respectively. A conversion of about 75% in the case of the former acid and about 80% in the case of the latter was noticed.

Action of Mercuric Chloride.—Acetyl coumaric acid (1 g.) was dissolved in 25 c.c. of rectified spirit and an equimolecular quantity of mercuric chloride was added. The resulting clear solution was refluxed on a water-bath for 3 hours. It was then diluted and allowed to stand, when coumarin mercuric chloride was deposited with its characteristic crystalline structure. After leaving overnight, the crystals were filtered and recrystallised from water. They came down as colourless needles melting at 164°. Mixed melting point with an authentic sample was not depressed. When boiled for about 5 minutes with dilute hydrochloric acid, the substance decomposed into coumarin melting at 70°. The yield was theoretical.

The result was similar when the experiment was repeated using water instead of alcohol as the solvent.

The other acetyl coumaric acids produced the corresponding coumarins in almost theoretical yields, when they were boiled with alcoholic or aqueous

solutions containing equimolecular quantities of mercuric chloride and subsequently treated with hydrochloric acid in order to decompose completely the mercuric chloride addition compounds.

Summary

The acetyl derivatives of coumaric, 4-methylcoumaric, 5-nitrocoumaric, psoralic and isopsoralic acids have been prepared and their behaviour studied under conditions which bring about *trans* to *cis* inversion. Under the influence of sunlight, the first three acids produce the corresponding coumarins on prolonged exposure. When heated to above their respective melting points all the acetyl compounds undergo inversion to an extent of 60–80%. Along with the pyrones, highly polymerised resinous compounds are also produced on heating. Treatment with equimolecular amounts of mercuric chloride in aqueous or aqueous alcoholic medium brings about inversion in all the cases with almost theoretical yields.

REFERENCES

1. Seshadri .. *Curr. Sci.*, 1934, **3**, 19.
2. ——— and Suryaprakasa Rao .. *Proc. Ind. Acad. Sci.*, (A), 1936, **3**, 293.
3. ——— .. *Ibid.*, 1936, **4**, 157.
4. Rangaswami and Seshadri .. *Ibid.*, 1937, **5**, 249.
5. Suryaprakasa Rao, Venkata Rao and Seshadri .. *Ibid.*, 1937, **6**, 148.
6. Tiemann and Herzfeld .. *Ber.*, 1877, **10**, 284.
7. Stoermer .. *Ibid.*, 1911, **44**, 651.
8. Dey, Rao and Seshadri .. *J.I.C.S.*, 1934, **11**, 743.
9. Roth and Stoermer .. *Ber.*, 1913, **46**, 268.

ON ISOTROPIC MANIFOLDS IN THE THEORY OF RELATIVITY

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The condition of isotropy has played a great part in the general theory of relativity in so far as it has considerably helped to obtain the solutions of Einstein's gravitational equations. It has been customary to take this condition as

$$T_1^1 = T_2^2 = T_3^3 = -p \tag{1}$$

which is found to be only an approximate relation. The condition for an isotropic manifold as understood in differential geometry is given by the equation

$$B^l_{ijm} = K\,(g_{im}\,\delta^l_j - g_{ij}\,\delta^l_m) \tag{2}$$

where the term on the left hand side is the Riemann-Christoffel tensor of the first kind for the fundamental tensor g_{ij}, and δ^i_j is the Krönecker delta. The relation (2) can be expressed in terms of Riemann-Christoffel tensor of the second kind as

$$B_{ijmn} = g_{nl}\,B^l_{ijm} = K\,(g_{im}\,g_{nj} - g_{ij}\,g_{nm}) \tag{3}$$

Here K is the Riemannian curvature which is, in general, supposed to vary from section to section of the space considered.

It is the object of this paper to study the isotropy of relativity manifolds from the point of view of differential geometry. It has been shown by Walker[1] that a Riemannian manifold V_n satisfying the condition of spherical symmetry about the geodesics of a V_{n-1} has the line-element of the form

$$ds^2 = dt^2 + g_{ij}\,dx'^i\,dx'^j, \quad (i, j = 1, 2 \cdots, n-1) \tag{4}$$

In general, we can write (4) as

$$ds^2 = g_{ij}\,dx\,dx^i\,dx^j, \quad (i, j = 0, 1, 2, \cdots, n-1) \tag{5}$$

where $g_{00} = 1$, $g_{0i} = g_{i0} = 0$, $g_{ij} = g'_{ij}$, $(i, j = 1, 2 \cdots, n-1)$.

It will be understood that V_{n-1} is characterised by the line-element

$$d\sigma^2 = g'_{ij}\,dx'^i\,dx'^j \tag{6}$$

The condition of isotropy for V_{n-1} can now be expressed as

$$B'^{l}_{ijm} = K' (g'_{im} \delta^{l}_{j} - g'_{ij} \delta^{l}_{m}) \tag{7}$$

It will be seen that for $(i, j, l, m = 1, 2, \cdots, n-1)$ the relations (2) and (7) are the same, for

$$\left.\begin{aligned} g_{ij} &= g'_{ij}, \\ B^{l}_{ijm} &= B'^{l}_{ijm}. \end{aligned}\right\} \tag{8}$$

Therefore,

$$K = K'. \tag{9}$$

Hence, we deduce that the necessary condition that V_n is an isotropic manifold is that V_{n-1} is also another isotropic manifold with the same Riemannian curvature as that of V_n.

Also from (2) we get, in addition

$$B^{0}_{ijm} = 0, \tag{10}$$

and

$$\left.\begin{aligned} B^{0}_{iom} &= K g_{im} \\ \text{or,} \quad g^{im} B^{0}_{iom} &= K \\ \text{or,} \quad g^{im} B^{0}_{iom} &= g^{jl} B^{0}_{jol} \end{aligned}\right\} \tag{11}$$

[The relations (10) and (11) can, otherwise, be proved as follows: We have

$$\begin{aligned} B^{0}_{ijm} &= -\tfrac{1}{2} \{im, a\} \frac{\partial g_{aj}}{\partial t} + \tfrac{1}{2} \{ij, a\} \frac{\partial g_{am}}{\partial t} - \tfrac{1}{2} \frac{\partial}{\partial t} \left[\frac{\partial g_{im}}{\partial x^{j}} - \frac{\partial g_{ij}}{\partial x^{m}} \right] \\ &= -\tfrac{1}{2} \frac{\partial}{\partial t} [mi, j] + \tfrac{1}{2} g_{aj} \frac{\partial}{\partial t} \{im, a\} + \tfrac{1}{2} \frac{\partial}{\partial t} [ji, m] \\ &\quad - \tfrac{1}{2} g_{am} \frac{\partial}{\partial t} \{ij, a\} - \frac{\partial}{\partial t} [ji, m] + \tfrac{1}{2} \frac{\partial}{\partial t} \left(\frac{\partial g_{jm}}{\partial x^{i}} \right) \end{aligned}$$

(from the properties of the three-index symbols),

$$\begin{aligned} &= \tfrac{1}{2} g_{aj} \frac{\partial}{\partial t} \{im, a\} - \tfrac{1}{2} g_{am} \frac{\partial}{\partial t} \{ij, a\} \\ &= 0, \text{ by the interchange of suffixes.} \end{aligned}$$

Similarly,

$$B^{0}_{ioj} = \tfrac{1}{4} g^{a\rho} \frac{\partial g_{i\rho}}{\partial t} \frac{\partial g_{aj}}{\partial t} - \tfrac{1}{2} \frac{\partial^2 g_{ij}}{\partial t^2};$$

and

$$g^{ij} B^{0}_{ioj} = \tfrac{1}{4} g^{ij} g^{a\rho} \frac{\partial g_{i\rho}}{\partial t} \frac{\partial g_{aj}}{\partial t} - \tfrac{1}{2} g^{ij} \frac{\partial^2 g_{ij}}{\partial t^2}.$$

Therefore,

$$g^{ij} B^{0}_{ioj} = g^{lm} B^{0}_{iom}.]$$

Equations (10) & (11) supply the sufficient conditions for the isotropy of V_n.

The Riemannian curvature K can now be expressed by the invariant relation of the form

$$K = \tfrac{1}{4}\, g^{ij}\, g^{\alpha\rho}\, \frac{\partial g_{i\rho}}{\partial t}\, \frac{\partial g_{\alpha j}}{\partial t} - \tfrac{1}{2}\, g^{ij}\, \frac{\partial^2 g_{ij}}{\partial t^2} \tag{12}$$

If we write

$$d\sigma^2 = U(t)\, f_{ij}\, dx^i dx^j, \tag{13}$$

where $g_{ij} = g'_{ij} = U(t)\, f_{ij}$, $(i, j = 1, 2, \cdots, n-1)$, and $g^{ij} = g'^{ij} = \frac{f^{ij}}{U}$, f^{ij} having the same significance as g^{ij}. It is explicitly assumed that the f_{ij}'s are not functions of t. For this case, therefore, (12) simplifies to

$$\tfrac{1}{4}\, \frac{\dot{U}^2}{U^2}\, f^{ij}\, f^{\alpha\rho}\, f_{i\rho}\, f_{\alpha j} - \tfrac{1}{2}\, f^{ij}\, f_{ij}\, \frac{\ddot{U}}{U} = K\,;$$

that is,

$$\tfrac{1}{4}\, \frac{\dot{U}^2}{U^2} - \tfrac{1}{2}\, \frac{\ddot{U}}{U} = K \tag{14}$$

where a dot denotes a differentiation with regard to t. The space being regarded as having a constant Riemannian curvature, K does not vary from point to point. The complete integral of (14) is of the form :

$$U = A^2 \cos^2 (\alpha + \sqrt{K}t) \tag{15}$$

where A and α are constants of integration. Therefore, the line-element for an isotropic Riemannian manifold having a spherical symmetry about the geodesics of a V'_{n-1} can be written as

$$ds^2 = dt^2 + A^2 \cos^2 (\alpha + \sqrt{K}t)\, f_{ij}\, dx^i dx^j \tag{16}$$

where V'_{n-1} is itself an isotropic manifold characterised by

$$d\sigma'^2 = f_{ij}\, dx^i dx^j. \tag{17}$$

We shall now apply these considerations to one of the most important line-elements in the theory of relativity satisfying the general conditions of spherical symmetry. This line-element is given by

$$ds^2 = H(r, t)\, dt^2 - F(r, t)\, \{dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2\} \tag{18}$$

For line-elements of the form (18), the condition of isotropy (2) reduces ultimately to relations of the type

$$\left.\begin{aligned} &g^{il}\, B^j_{ijl} = g^{ll}\, B^m_{lml}, \\ \text{and} \quad &B^l_{ljm} = -K g_{lj}\, \delta^l_m, \ (l \neq j, \ i \neq m). \end{aligned}\right\} \tag{19}$$

Now, if we apply the process of contraction of tensors to the relations (19) we get

$$\left.\begin{aligned} &G = G, \\ \text{and} \quad &G_{ij} = -K g_{ij}. \end{aligned}\right\} \tag{20}$$

For cosmological considerations, Einstein has chosen

$$G_{ij} = \lambda g_{ij} \tag{21}$$

as the modified law of gravitation, where λ is the cosmical constant. Comparing (21) with the second equation (20), we see that Riemannian curvature is given by $K = -\lambda$. It will, therefore, be evident that the modified law of gravitation is implied in the condition of isotropy as understood in Differential Geometry. $K = 0$ gives the original law of gravitation.

For a perfect fluid (or, a disordered radiation which is the same as a perfect fluid), the material-energy tensor can be expressed as

$$T^{ij} = (\rho_0 + p)\, v^i v^j - p g^{ij} \tag{22}$$

which gives the scalar

$$T = g_{ij} T^{ij} = \rho_0 - 3p = \rho_{00} \tag{23}$$

denoting the invariant density ρ_{00}. In the present case we must have $\rho_0 = 3p$. Consequently, the invariant density vanishes, and, we deduce the following relation

$$T_1^1 = T_2^2 = T_3^3 = -p \tag{24}$$

just as in the case of proper co-ordinates. Equations (24), therefore, give us the usual (physical) condition of isotropy. As a consequence of (24), it will be found that $v^1 = v^2 = v^3 = 0$, and $T_1^0 = 0$. This puts a sort of restriction of the field given by (18). It might be contended that this is a very severe restriction because the cross-component of the T^i_j denoting the flow of matter from within or without the model vanishes. But the model in question is supposed to cover all the material limits of the universe at a particular epoch, so that, flow of matter from beyond or beyond these limits does not arise at all. Moreover, the internal motion is given by the geodesic equations, and not by T_1^0.

Considering the tensor expression (22), we may say that the idea of isotropy is inherently present in it in so far as (22) is derived from the law of gravitation (21). For the line-element (18), the surviving components of the material-energy tensor satisfy the following relation :

$$H (T_1^0)^2 + F (T_2^2 - T_0^0) (T_2^2 - T_1^1) = 0^{(2)} \tag{25}$$

which has been chosen by Walker as the condition of isotropy. This relation does not give isotropic pressure (*i.e.*, the physical condition of isotropy) unless $T_1^0 = 0$. While, by a simple process and assumptions not inconsistent with physical ideas we have deduced the extra condition of isotropy (24). This goes to point out that (25) is not at all any real condition of isotropy.

REFERENCES

1. " On Riemannian spaces with spherical symmetry about a line, and the conditions for isotropy in General Relativity, " *Quart. Jour. Maths.* (Oxford series), **6**, 22, p. 87, Eq. 32.

2. *Loc. cit.*, p. 89, Eq. 45.

THE CONDENSATION OF ALDEHYDES WITH AMIDES

Part IV. Of *m*-Hydroxybenzaldehyde

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THE condensation of salicylaldehyde with amides has been already described[1] in which the products were all salicylideneamides, and possessed certain peculiar physical properties (*loc. cit.*). The use of pyridine in traces as a condensing agent gave excellent yields, which were often quantitative. Similar condensations with the isomeric *m*- and *p*-hydroxybenzaldehydes have, so far as is known to us, never been studied. These studies are described here and in the next paper.

m-Hydroxybenzaldehyde combines with amides to give products of a similar constitution, namely the *m*-hydroxybenzylideneamides, but there are certain peculiar features of the reaction which are in contrast with the behaviour observed in the case of salicylaldehyde. Since, in the case of all the condensations studied with salicylaldehyde, the yields were uniformly inferior both in quality and in quantity when sodium acetate was used as a condensing agent to those obtained by means of a trace of an organic base, in the present case the condensations were carried out exclusively by means of a trace of an organic base. Preliminary observations, however, showed definitely that the presence or absence of a trace of the base had not the same significance here that it had in the salicylaldehyde-condensations : in other words, the condensation readily took place even in the absence of any condensing agent (as in the case of salicylaldehyde), but the trace of pyridine or lutidine or so, when present, did not materially increase the yield, and was apparently responsible for some resinification (contrast).

Again, while salicylidene-formamide was obtainable in quantitative yields,[1] from formamide and salicylaldehyde, no pure product could be separated from *m*-hydroxy-benzaldehyde and formamide, even in the presence of a trace of pyridine or of lutidine under a variety of conditions of heating and of temperature. Acetamide also did not condense, though propionamide, benzamide and phenylacetamide gave the usual type of

products. The yields in the three cases were materially improved by taking the aldehyde and the amide in 1 : 2 mol. proportions, which did not affect the nature of the product.

The products were, always, only the unsaturated benzylidene-amides and not the saturated bisamide in any case. The best yield did not exceed 58% of the theoretical.

The three products were either colourless or lightly coloured, were recrystallised easily and gave good melting-points as well as good analyses.

Experimental

m-*Hydroxybenzylidenepropionamide.*—*m*-Hydroxybenzaldehyde 3 g. and propionamide 1·8 g. (1 : 1 mol.) were heated on a boiling water-bath till fusion to a homogeneous liquid, when the heating was continued at 80–85° for six hours. The viscous mass, dark brown in colour, on cooling, partially solidified. It was washed with cold dilute alcohol, and the residue was crystallised from dilute alcohol. Pale yellow crystals, melted at 210° C., and weighed 0·7 g.

In another experiment the aldehyde 3 g. was heated with 3·6 g. of the amide (1 : 2 mol. proportions) and the product, taken out in the same way, weighed 1·2 g. (27·5%). Found : N = 7·79% ; $C_{10}H_{11}O_2N$ requires N = 7·91%.

m-*Hydroxybenzylidenebenzamide.*—The aldehyde 3 g. and benzamide 3 g. (1 : 1 mol.) were heated on an oil-bath at 110–15° for three hours. At 95° the mass fused to a homogeneous liquid and water vapours were given off. The colour gradually became dark brown. When cold, the mass was still plastic. It was treated with hot alcohol, when, on cooling, buff coloured crystals were obtained, which, on recrystallisation from hot alcohol, gave pure milk-white crystals, m.p. 205° (1·2 g.).

In another experiment, the initial heating was at 100° and, after fusion, at 80° for six hours. The reaction-product was slightly orange in colour, was cooled overnight, was found to be a hard solid orange mass next morning, and was crushed and purified by means of alcohol as before. The yield after this low-temperature and longer heating was higher, 1·8 g.

The substances were taken in 1 : 2 mol. proportions (3 g. aldehyde and 6 g. amide) and heated at first at 100° and then at 90° for eight hours. The mixture became brown, but on treating it as usual the yield increased to 3·2 g. (*i.e.*, 58% nearly). (Found : N = 5·79, 5·82%. $C_{14}H_{11}O_2N$ requires N = 6·22%.) Molecular weight by Rast's method, using camphor,

gave M = 234 : *m*-hydroxybenzylidenebenzamide requires 225, while the bisamide requires 346.

m-*Hydroxybenzylidene-phenylacetamide.*—1·5 g. of the aldehyde and 3·4 g. of phenylacetamide (1 : 2 mol.) were heated on a water-bath for four hours. The mixture fused and gradually turned dark brown as heating went on. On cooling, the resinous mass was extracted with ether, and the residue was recrystallised from hot dilute alcohol or acetone. Buff-coloured needles melting at 190°. 1·2 g. or 40% yield. Found : N = 5·73% ; $C_{15}H_{13}O_2N$ requires N = 5·85%.

Condensations were attempted with acetamide, in the presence of a trace of pyridine or of lutidine, as well as in the absence of a condensing agent, and temperatures ranging from 50° to 130° C. were tried. In most cases much resinification was observed and some of the aldehyde was recovered unchanged. The same was observed when formamide was heated with *m*-hydroxybenzaldehyde.

The three condensation products obtained resembled the corresponding salicylidene-amides, in declolourising immediately Baeyer's reagent, in giving a colour with concentrated sulphuric acid and in being decomposed to the original aldehyde when heated with strong mineral acids.

Summary

m-Hydroxybenzaldehyde condenses when heated alone with propionamide, benzamide and phenylacetamide, giving corresponding *m*-hydroxybenzylideneamides, which have been described. No condensation product was obtained with acetamide or formamide.

The thanks of the authors are due to the Government of the United Provinces for the grant of a Government Research Scholarship to one of us (R. K. M.) which has enabled him to take part in this work.

REFERENCE

1. Pandya and Sodhi .. *Proc. Ind. Acad. Sci.*, 1938, (A), **7**, 361.

THE CONDENSATION OF ALDEHYDES WITH AMIDES

Part V. Of *p*-Hydroxybenzaldehyde

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p-Hydroxybenzaldehyde condenses readily with formamide, acetamide, propionamide, benzamide and phenylacetamide, and the products are the corresponding *p*-hydroxybenzylidene-amides, as in the cases of the *o*- and *m*-hydroxybenzaldehydes[1,2]. The condensations are brought about by heating the aldehyde with the amide for 4–5 hours at 130°–140°, in the presence or absence of a trace of organic bases like pyridine and piperidine. The presence of the base improved the yield only slightly (contrast salicylaldehyde,[1] and compare *m*-hydroxybenzaldehyde[2]). The yields, however, were uniformly very good, never being less than 60% of the theoretical, and reaching up to 92% as the highest, being in this respect more like those of the *o*- than those of the *m*-hydroxybenzylidene-amides.[1] In physical properties, too, they bore a very strong resemblance to them, being more or less yellow in colour, looking when cold in the reaction-flask, like ' organic glass ' and having on the whole very limited solubilities in the usual organic solvents. They did not give a sharp melting point, but generally decomposed before reaching it. The constancy of this point, after repeated crystallisations or precipitations, and the agreement of the analytical figures showed the purity.

As before, they all instantly decolourised Baeyer's reagent, and gave a deep red coloration with concentrated sulphuric acid.[1,2] They also gave a pink coloration with strong hydrochloric acid, which became deep rose on warming or on keeping. On heating, with strong mineral acids, they decomposed with the liberation of the original aldehyde.

Experimental

p-*Hydroxybenzylidene-acetamide.*—3 g. *p*-hydroxybenzaldehyde and 1·5 g. acetamide were taken, with 0·19 g. pyridine (1 : 1 : 0·1 mol.), and heated in an open flask in an oil-bath at 130–40° ; the reacting mixture fused at 100–15° with liberation of water-vapours. After 4 hours, the

heating was stopped, and about 30 c.c. of alcohol were added to the cold flask, and the whole was left overnight. The insoluble portion was filtered off, the filtrate concentrated by evaporating the alcohol to half the bulk and cold water added which produced a precipitate. The whole was acidified with a little dilute hydrochloric acid ; the precipitate collected and washed with water. When dry it weighed 3·7 g. (yield 92%).

It was a yellow powder, which was insoluble in hot or cold water, ether, chloroform or benzene, slightly soluble in acetone, and very easily soluble in alcohol, methyl alcohol and pyridine. It also dissolved readily in dilute alkali solution from which it could be reprecipitated by the addition of some dilute hydrochloric acid. It failed to come out in crystals from any one solvent or a mixture of solvents ; it was purified by repeated precipitations (acetone and water) and washing with ether to remove any unchanged aldehyde that might have remained. It did not melt even till 340° but became dark brown showing decomposition had set in.

When piperidine was substituted (0·21 g.) in place of pyridine, and, also when no base was used, and the other conditions were unchanged, the yield in each case was 3·5 g. or 87·5%. Found nitrogen = 9·02% ; $C_9H_9NO_2$ requires 8·59%.

p-*Hydroxybenzylidene-formamide.*—3 g. aldehyde, 1 g. formamide and 0·285 g. pyridine (1 : 1 : 0·15 mol.) were mixed in a flask. In a preliminary experiment, to avoid decomposition of formamide, which boils at 105°, the heating was done on a water-bath for 8 hours : but this gave the unchanged aldehyde only. The heating was, therefore, done in an oil-bath at the usual temperature of 130–40° for 4 hours, and when the contents were cold, methyl aclohol was added and the whole was left overnight. The product was taken out as before by partial concentration of the filtrate and subsequent addition of acidulated water. Yield 2·3 g. or 63%. The crude product was washed with ether and acetone, dissolved in aqueous acetone and reprecipitated by addition of excess of acetone. This was repeated several times, till the dark yellow product decomposed, without melting, at the constant temperature 216°. Its solubility was similar to that of the acetamide compound described above. It also gave the same reactions. With piperidine in place of pyridine, the yield was the same, 2·3 g., while in the absence of any base the yield was little less, 2·2 g. about 60%. Found N = 8·82% ; $C_8H_7NO_2$ requires 9·30%.

p-*Hydroxybenzylidene-propionamide.*—The aldehyde (3 g.), propionamide (1·8 g.) and pyridine in a trace as before, were heated for 5 hours at 140°. The product was taken out in the usual way and weighed 3·6 g.

Yield 84%. It was dirty white, was purified by means of alcohol and water, washing at the end with ether and warm water. It decomposed at 195°.

Its behaviour was similar to that of the other derivatives described above. Piperidine in place of pyridine gave the same yield (84%), while in the absence of any base the yield was 3·5 g. or about 82%. (Found N = 7·898% ; $C_{10}H_{11}O_2N$ requires 7·909%.)

p-*Hydroxybenzylidene-benzamide.*—3 g. aldehyde, 3 g. benzamide and pyridine in a trace (1 : 1 : 0·15 mol.) were heated at 140° for five hours, and the product was extracted with ethyl aclohol as before and precipitated by the addition of excess of water to the concentrated extract. The yield was 4·5 g. or 81%. With piperidine the yield was 4·6 g. or 83%. When no base was present, the yield was also 81%. Its solubilities, properties and reactions were similar to those described above. The crude product was yellow-brown, but the colour became lighter under the usual method of purification. It did not melt, but became dark red at 190° and swelled at about 215°. (Found N = 5·86% ; $C_{14}H_{11}NO_2$ requires 6·22%.)

p-*Hydroxybenzylidene-phenylacetamide.*—3 g. aldehyde, 3.3 g. phenylacetamide and pyridine (1 : 1 : 0·1 mol.) were heated in the usual way, and gave 4·8 g. or 81% yield. In the absence of any base the yield was 4·7 g. or 80%.

It was lemon-yellow in colour, did not melt even up to 340° though the colour was gradually darkening, indicating decomposition. (Found N = 6·07% ; $C_{15}H_{13}NO_2$ requires 5·86%.)

Thanks are due to Mr. Rup Kishore Mehra who carried out some of the nitrogen-determinations.

Summary

p-Hydroxybenzaldehyde condenses with all the five amides easily, giving very good yields of the corresponding *p*-hydroxybenzylidene-amides, which resemble closely the products obtained from the condensation of salicylaldehyde (rather than those obtained from *m*-hydroxybenzaldehyde).

REFERENCES

1. Pandya and Sodhi .. *Proc. Ind. Acad. Sci.*, (A), 1938, **7**, 361.
2. Mehra and Pandya .. *Ibid.*, (A), 1939, **10**, 279.

THE CONDENSATION OF ALDEHYDES WITH AMIDES

Part VI. The Condensations of *o*-, *m*- and *p*-Methoxybenzaldehydes

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CONDENSATIONS of *o*-, *m*- and *p*-hydroxybenzaldehydes with a few aliphatic and aromatic acid amides have already been reported.[1,2,3] In the present paper are described the condensations of the same amides with the three corresponding methyl ethers of the three hydroxyaldehydes.

The results have been somewhat different from what had been expected. In the first instance, under the experimental conditions employed, formamide gave little or no condensation product, in spite of repeated attempts under different temperatures and in the presence as well as in the absence of an organic base. Of the three hydroxybenzaldehydes, the *m*-aldehyde could not be condensed with this amide,[2] the *para*-isomer had condensed to give an yield of 63%,[3] and salicylaldehyde had actually given a quantitative yield.[1]

Secondly, while all the three hydroxybenzaldehydes had formed with the amides compounds of the type of unsaturated benzylidene-monoamides, the products of condensation of the methoxybenzaldehydes were all benzylidene-bis(or di-)amides, that showed no sign of unsaturation.

The yields in the present case were between 37% and 57%, and were slightly better than those of *m*-hydroxybenzylidene-amides, but were not so good as those of the corresponding *o*- and *p*-derivatives.

The presence of the organic base in a trace made little improvement in the yields.

The methoxy-benzylidene-bisamides, though not obtained in very high yields, were on the whole easily purified, gave good melting points, and had the chemical character that is expected of such compounds. In several cases it was possible to determine molecular weights by Rast's method and these values obtained were in conformity with the expected values of the bis-compounds.

Experimental

o-*Methoxybenzylidene-bisacetamide.*—3·4 g. *o*-methoxybenzaldehyde, 4·5 g. acetamide and 0·22 g. pyridine (1 : 3: 0·15 mol.) were heated on an oil-bath at 130° for 4 hours. The mass fused at about 100° and began to give off vapours of water. The cold solid mass was found to contain very appreciable amounts of the unreacted aldehyde, which was removed by extractions with ether. The remaining solid was crushed and well digested with water to remove acetamide, and filtered off. On recrystallisation from hot alcohol, the bisacetamide came out in milk-white needles, m.p. 223°. Yield 2·2 g. or 37% of theory.

The *o*-methoxybenzaldehyde and acetamide, in the same amounts as above, but without pyridine or any other condensing agent, were also heated for 8 hours at 100°, the product recovered as above and the yield was found to be 2·8 g. or 47%. In another experiment, the heating was carried out, in the absence of a condensing agent at 130–40° for 4 hours, when the yield was 2·9 g. or 49%. (Found N = 11·92% : the bisamide $C_{12}H_{16}O_3N_2$ requires 11·87 %.)

o-*Methoxybenzylidene-bispropionamide.*—3·4 g. *o*-methoxybenzaldehyde and 3·6 g. propionamide (1 : 2 mol.) were heated alone on an oil-bath at 110–15° for 4 hours, and the product taken out as before. Recrystallised from alcohol or acetone, the white silky needles weighed 2·5 g. (38% yield), and melted at 196–97°. (Found N = 10·88% : the bisamide $C_{14}H_{24}O_3N_2$ requires 10·60%.)

o-*Methoxybenzylidene-bisbenzamide.*—3·4 g. *o*-methoxybenzaldehyde and 6 g. benzamide (1 : 2 mol.) were heated on an oil-bath at 130–35° for 4 hours. The product was separated as before, recrystallised from hot alcohol or acetone, and came out in white micro needles melting at 233°. The yield was 5·2 g. or about 58%. (Found N = 7·97% : the bisamide $C_{22}H_{20}O_3N_2$ requires N = 7·78%.) Molecular weight, Rast's method—Found : 367·6 and 359·8, Calc. 360.

o-*Methoxybenzylidene-bisphenylacetamide.*—1·7 g. of *o*-methoxybenzaldehyde and 3·4 g. of phenylacetamide (1/80th mol. 1 : 2 mol. proportion) were heated together as usual for 4 hours at 130–40°. The product, taken out as before and recrystallised from hot dilute alcohol or acetone, came out in white silky needles, melting at 197°, and weighing 2·7 g. : yield = 55·7%. (Found N = 7·33% ; the bisamide $C_{24}H_{24}O_3N_2$ requires 7·22%.)

Condensation of o-*methoxybenzaldehyde with formamide*—was attempted under a variety of conditions, but in all cases the aldehyde was recovered

unchanged and some resin was obtained from which no definite product could be separated.

m-*Methoxybenzylidene-bisacetamide.*—Although acetamide was not found to undergo condensation with *m*-hydroxybenzaldehyde,[2] it combined readily with its methyl ether. 3·4 g. *m*-methoxybenzaldehyde and 4·5 g. acetamide (1 : 3 mol. proportion) were heated on an oil-bath at 115–20° for 4 hours, and the *m*-methoxy benzylidene-bisacetamide was taken out in the usual way. It could be recrystallised from hot water, or better, from hot alcohol or acetone. It came out in white silky needles, weighed 3·2 g. (yield = 54%) and melted at 206°. (Found: N = 11·88%; the bisacetamide $C_{12}H_{16}O_3N_2$ requires 11·87%.)

m-*Methoxybenzylidene-bispropionamide.*—3·4 g. of the *m*-methoxybenzaldehyde and 3·6 g. of propionamide (1 : 2 mol.) were heated at 110–15° for 4 hours, the product separated as usual and recrystallised from hot alcohol or acetone. It weighed 3·4 g. (yield = 51·5%), m.p. 201°. (Found: N = 10·92%; the bisamide $C_{14}H_{20}O_3N_2$ requires 10·60%. Molecular weight, found by Rast's method = 263·3, calc. 264.)

m-*Methoxybenzylidene-bisbenzamide.*—3·4 g. *m*-methoxybenzaldehyde and 6 g. benzamide were heated in an oil-bath at 135–40° for 4 hours and the solid separated and purified as usual. The product, recrystallised from hot alcohol or acetone, came out in white needles and weighed 4·7 g. (yield = 52%), m.p. 201–02°. (Found N = 7·86%; the bisamide $C_{22}H_{20}O_3N_2$ requires 7·78%.)

m-*Methoxybenzylidene-bisphenylacetamide.*—1·7 g. of *m*-methoxybenzaldehyde and 3·4 g. of phenylacetamide were heated at 130–40° for 4 hours, and the product separated and purified as usual. Recrystallised from hot alcohol or acetone, it came out in white needles, melted at 181–82°, and weighed 2·5 g. (yield = 51·5%). (Found: N = 7·42%; the bisamide $C_{24}H_{24}N_2O_3$ requires 7·22%.)

From formamide-condensation, unchanged aldehyde and resin were obtained.

p-*Methoxybenzylidene-bisacetamide.*—3·4 g. anisaldehyde and 4·5 g. acetamide (1 : 3 mol.) were heated at 120–25° for 4 hours and the product treated as before. Recrystallised from hot alcohol or acetone, it melted at 230–31° and weighed 3·2 g. (yield = 54%). It was milk-white needled crystals. (Found N = 12·28%: the bisamide $C_{12}H_{16}O_3N_2$ requires 11·87%.)

p-*Methoxybenzylidene-bispropionamide.*—3·4 g. anisaldehyde and 3·6 g. propionamide (1 : 2 mol.) were heated for 4 hours at 110–15°, and the

resulting product separated and purified as usual. It came out in white needles when recrystallised from hot alcohol or acetone, melted at 228° and weighed 2·7 g. (yield = about 40%). (Found: N = 10·77%; the bisamide $C_{14}H_{20}O_3N_2$ requires 10·60%.)

p-*Methoxybenzylidene-bisbenzamide.*—3·4 g. anisaldehyde and 6 g. benzamide (1 : 2 mol.) were heated at 130–35° for 4 hours and the resulting product separated and purified as usual. Recrystallised it came out as white microcrystalline powder, melting at 223–224° and weighing 4·2 g. (yield = about 47%). Found: N = 7·37%; the bisamide $C_{22}H_{20}O_3N_2$ requires 7·78%.)

p-*Methoxybenzylidene-bisphenylacetamide.*—1·7 g. anisaldehyde and 3·4 g. phenylacetamide (1 : 2 mol.) were heated for 4 hours at 130–40°, and the product recovered and purified in the usual way. It came out in white silky crystals, melted at 243°, and weighed 2·7 g. (yield = about 56%). (Found N = 7·407%; the bisamide $C_{24}H_{24}O_3N_2$ requires 7·22%.) Found molecular weight (Rast) = 377·3, calculated = 388. With formamide after several failures, anisaldehyde yielded some pale yellow crystals, melting at about 171°, which might be the condensation product. But its amount was too small for full investigation.

It is hoped to investigate the formamide condensations of several of these aldehydes more thoroughly some other time.

Our thanks are due to the Government of the United Provinces for the grant of a Research Scholarship to one of us (R. K. M.) which has enabled him to take part in this work.

Summary

Condensations of the three *o*-, *m*- and *p*-methoxybenzaldehydes with certain amides show that formamide does not condense with any of them to an appreciable extent, under the conditions employed, and that the other amides react easily giving corresponding methoxybenzylidenebisamides.

REFERENCES

1. Pandya and Sodhi .. *Proc. Ind. Acad. Sci.*, 1938, (A), **7**, 361.
2. Mehra and Pandya .. *Ibid.*, 1939, (A), **10**, 279.
3. Manzur and Pandya .. *Ibid.*, 1939, (A), **10**, 282.

STUDIES IN COLLOID OPTICS

III. Scattering of Light by Stearic Acid Hydrosols and by Sodium Stearate Sols and Gels

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Introduction

THE colloid chemistry of fatty acid hydrosols offers an extremely interesting field of study which has not been explored in great detail, although surface films of these materials on water have been extensively studied by Langmuir, Adam and others. These hydrosols, when prepared under suitable and properly controlled conditions, furnish very simple if also not very stable (except in presence of stabilizing agents) systems which are very useful for studies on the nature of interfaces.

One of the common methods of preparing these fatty acid hydrosols is by pouring an alcoholic solution of the acid into water, and subsequently removing the alcohol from the system. By adopting this method, Iyer and Iyengar[1] have successfully prepared appreciably stable sols of stearic acid and also discussed in some detail the conditions of their formation and stability. Iyer has also utilised these sols for studies on the mechanism of neutralisation at interfaces by means of potentiometric[2] and conductometric[3] titrations.

The colloid chemistry of soaps has been a widely investigated field of study at the hands of numerous investigators amongst whom particular mention may be made of McBain and his collaborators.[4] The large variety of soaps available, the different types of sols and gels they form and the remarkable changes in properties of solutions which accompany the variations in tempe rature and concentration, have formed the basis of a large number of investigations. Particular interest however attaches to the dilatometric investigations of Heymann[5] on the sol-gel-curd transformation of sodium oleate solutions, his general conclusions being that the molecules of the clear jelly or sol are more loosely packed than in the microcrystals of the curd.

In the course of the present investigation an attempt has been made to study, by optical means, the changes which take place when a stearic acid hydrosol is heated. A study has also been made, through light scattering methods, of the sol-gel transformation of sodium stearate solutions in water.

Experimental

Preparation of the Stearic Acid Sol.—Kahlbaum's pure stearic acid, further purified by recrystallisation, was employed in the preparation of the sol. Methyl alcohol purified by distillation over caustic potash and double distilled conductivity water stored in Jena glass vessels were used in the experiments.

A solution of stearic acid in methyl alcohol was prepared in the cold and poured into about five times its volume of boiling water. The boiling of the solution was then continued for a long time (12–24 hours) to remove the alcohol as completely as possible, water being frequently added to make up for loss by evaporation. The sol was then cooled, filtered to remove any suspended material, and stored in Jena glass bottles. This sol was found to be stable for several weeks. As far as possible only freshly prepared sols were used in the experiments.

"Schlieren-Effect"—Stream Double Refraction.—The hydrosols of stearic acid showed in a very striking way the phenomenon of stream double refraction, or more correctly " Schlieren-effect " when subjected to disturbance. This double refraction was only of the mechanical type and was evidently caused by asymmetry in the shape of the micelles. Ultramicroscopic examination of the sol confirmed this view and showed the presence of micelles in the form of elongated rods.

In the course of investigations on these sols it was observed by the author and K. S. G. Doss[6] that when the sol was heated this phenomenon of Schlieren-effect disappeared very suddenly. On subsequent cooling it did not reappear immediately but did so only after standing for a considerable time, preferably overnight. Preliminary experiments by the same authors, with somewhat imperfectly purified sols (the methyl alcohol not being completely removed) indicated that the disappearance takes place quite sharply at a definite temperature but this temperature was not very reproducible with different sols and was also appreciably lower than the melting point of solid stearic acid. Later experiments with highly purified sols, carried out by K. S. G. Doss and M. P. V. Iyer[7] definitely indicated that it was more readily reproducible and more closely approximating to the melting point of pure stearic acid. The average temperature of disappearance of the Schlieren-effect was found by these authors to be 66·8° C. ± 0·5, this temperature being only slightly lower than the melting point of pure stearic acid, namely 69° C. Evidently the slight non-reproducibility of the results is due to the inability to prepare sols entirely free from methyl alcohol or even containing the same amount of alcohol in all cases.

Light Scattering by Stearic Acid Sols.—To obtain further information regarding the nature of the transition which occurs when stearic acid sols are heated, experiments were carried out on the scattering of light by these sols at different temperatures, and the usual depolarisation factors ρ_u, ρ_v and ρ_h (with unpolarised, vertically polarised and horizontally polarised incident beams of light) were determined. The experimental arrangement was the same as shown in Fig. 1 in a previous communication[8] with the following modification. The wooden box (' F ') in the figure was substituted by a metal box made of copper sheets and provided with windows of strain-free glass for observation purposes. This was filled with water and heated electrically by means of a nichrome coil surrounding the box. The sol was placed in a rectangular glass cell at the centre of the box and the temperature of the bath was altered slowly, depolarisation measurements being made at intervals. The results obtained in a typical case are shown in Table I below. Only white light was used in the experiments.

TABLE I

Depolarisation of light scattered by stearic acid hydrosol

Temperature	Depolarisation of scattered light		
	ρ_u %	ρ_v %	ρ_h %
25 °C.	7·7	2·2	33·4
35	8·2	2·2	27·1
55	8·2	2·2	26·0
60	9·1	2·5	24·9
63	8·2	2·0	24·9
65	7·7	1·9	23·8
67	8·2	2·0	21·8
69	7·2	1·5	20·8
71	7·2	1·3	18·9
75	5·8	1·3	16·3
80	7·2	1·5	16·3
90	13·3	1·1	16·3

The transition occurs in the neighbourhood of 69° C. Dilution of the sol did not have any appreciable effect on the depolarisation factors.

On cooling the sol it was found that the results could not be reproduced in the reverse order and even after the lapse of a considerable time the value of ρ_h persisted in being appreciably lower than in the original, unheated sol.

Sol-Gel Transformation of Sodium Stearate Solutions.—Pure sodium stearate (Kahlbaum) was dissolved in hot water to give solutions of the desired concentration, and the depolarisation factors ρ_u, ρ_v and ρ_h, of the light scattered by these solutions at different tempertures were determined in a way similar to that of the stearic acid sols. Observations on the intensity of the scattered light were also made in a qualitative manner. Table II shows the experimental results obtained in the case of a 2·5% solution.

TABLE II

Scattering of light by 2·5% sodium stearate solution

Temperature	Depolarisation of scattered light			Intensity of scattered light	Other observations
	ρ_u%	ρ_v%	ρ_h%		
90 °C.	8·2	1·8	49·0		
80	10·6	2·5	40·9		
70	13·3	3·1	37·6	System becomes opalescent	Highly viscous
60	13·3	3·1	33·4	Opalescence increases	Increased viscosity
50	14·7	3·4	27·1	Further increase in opalescence	Very high viscosity
42	16·3	4·1	13·2	Very high intensity of scattering	Rigid gel formed

The gel formed was of the opaque and curdy and not of the transparent type. The depolarisation could not be measured below 42° C. on account of the high scattering intensity of the system. With 1% sodium stearate sols similar results were obtained but the scattering intensity was lower. Also gelation of the systems occurred at a lower temperature.

Discussion

The phenomenon of stream double refraction or Schlieren-effect observed with stearic acid hydrosols is due only to the rod-like structure of the micelles. When the sol is subjected to mechanical disturbance such as flow, the forces of friction favour the orientation of these micelles with their long axes parallel to the direction of flow and thus cause the twinkling and double refraction effects. The abrupt disappearance of the effect on heating is clearly due to the melting of stearic acid and the consequent rearrangement in the shape of the micelles ; in other words, the stearic acid sol is converted to a stearic acid emulsion. In the case of highly purified sols, the temperature at which this transition occurs is practically the same as the melting point of solid stearic acid, but in imperfectly purified sols, where the methyl alcohol is not completely removed, the melting point of the micelles is lowered and the transition occurs at a considerably lower temperature. The slight non-reproducibility of the transition point in the purer sols is clearly due to traces of methyl alcohol which cannot be removed completely from the system. In fact Iyer and Iyengar[1] have stated that the presence of alcohol in traces is essential to the stability of the sol. It is however only natural to expect that a significant change in the shape of the micelles should be accompanied by simulataneous changes in the other physical properties of the system.

Light scattering studies have thrown very interesting light on the nature of this suspension-emulsion transition. The continuous decrease in the value of ρ_h on heating indicates a growth in micellar size due probably to partial heat coagulation. This growth is considerably intensified after the transition stage. The extremely low values of ρ_h also indicate that the micelles in the emulsion are larger than those in the suspension. As is only to be expected, this increased micellar size persists even after the subsequent cooling of the sol.

The variation of ρ_v below the transition temperature is slight. During the transition it becomes smaller but does not fall to the value zero. Further heatling records only slight variations. These results furnish proof that at the transition temperature the micelles become less asymmetrical and tend to assume a spherical shape but do not actually become spherical. The latter is a surprising conclusion because emulsions have so far been considered to consist of only spherical micelles. Presumably the polar nature of stearic acid does not allow the formation of spherical micelles even in the liquid state. It would be interesting to recall here that a similar observation regarding castor-oil emulsions was made by Subbaramaiya[9]

but the finite value of ρ_v therein was later attributed by Krishnan[10] to the existence of secondary scattering in the system. This explanation however fails in the present case because the scattering intensity is quite low.

The results obtained with sodium stearate sols show the presence, at a temperature of 90° C., of appreciably large micelles of sodium stearate possessing a high degree of asymmetry, thus clearly demonstrating the existence of neutral micelles in considerable proportion even at high temperatures. When the sol is cooled the ρ_h value falls rapidly thus showing a continuous increase in micellar size. A simultaneous increase in ρ_v also points to the increasing asymmetry in the shape of the micelles. At a temperature of 70° C. the liquid becomes opalescent and highly viscous. This may be taken to indicate the beginning of the formation of sodium stearate fibrils from the micelles. On further cooling the opacity and viscosity of the system continue to increase rapidly and at a temperature of 42° C. the system sets to a rigid, curdy gel. The micellar size at this stage is extremely large and the asymmetry in shape is also very high. Evidently the fibril formation is nearly complete and the elongated chain-like micelles intertwine amongst themselves to produce an immobile gel. The scattering intensity at this stage is also very high and depolarisation measurements can only be made with difficulty. These conclusions based on light scattering evidence are similar to those obtained by McBain and others from studies on other physical properties of soap solutions.

In conclusion, the author expresses his grateful thanks to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his keen and helpful interest in the work.

Summary

The investigations carried out on stearic acid hydrosols demonstrate that the phenomenon of Schlieren-effect exhibited by the sols is due to the presence of rod-like micelles and disappears on heating. The transition temperature is sharply defined, and in highly purified sols, is nearly the same as the melting point of solid stearic acid. In imperfectly purified sols however the transition occurs at a considerably lower temperature. The importance of the transition point as indicating a change from the solid to the liquid state of the micelles is pointed out. The phenomenon is not strictly reversible on cooling.

Light scattering studies on stearic acid sols have established that their micellar size is appreciably large and increases continually on heating, due probably to partial coagulation by heat. The asymmetry in the shape of

the micelles is high at low temparatures, and shows a fall at the transition point. At no stage however do the particles become truly spherical.

Studies on light scattering by sodium stearate sols have shown that on cooling a hot sol the micelles grow in size very rapidly and also exhibit enhanced asymmetry. The intensity of the scattered light also increases and becomes very high on gel formation. It is concluded that the micelles join together to form elongated chains which eventually lead to the formation of fibrils and a curdy opaque gel. The temperature of gelation is a function of the concentrantion of the sol.

REFERENCES

1. M. P. V. Iyer and H. R. Iyengar — *Jour. Mys. Uni.*, 1932, **6**, No. 1.
2. M. P. V. Iyer .. *Ibid.*, 1932, 6, No. 2.
3. ———— .. Unpublished.
4. McBain, *et al.* .. *J.C.S.*, 1932, **121**, 622; 1921, 1381; *J.A.C.S.*, 1928, **50**, 1636.
5. E. Heymann .. *Trans. Farad. Soc*, 1938, **34**, 689.
6. K. SubbaRamaiah, M. P. V. Iyer and K. S. G. Doss — *Curr. Sci.*, 1939, **8**, 360.
7. K. S. G. Doss and M. P. V. Iyer — Unpublished.
8. K. SubbaRamaiah .. *Proc. Ind. Acad. Sci.*, 1937, **5A**, 128.
9. D. S. Subbaramaiya .. *Ibid.*, 1934, **1A**, 709.
10. R. S. Krishnan .. *Ibid.*, 1938, **7A**, 98.

EINIGE NUMERISCHE IDENTITÄTEN

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1. Im *Boletin Matematico* (Buenos Aires), 1935, 4/5 gab ich einzelne Lösungen der Relation $\sum_{i=1}^{6} A_i^n = \sum_{i=1}^{6} B_i^n$ für $n = 1, 2, 3, 4$ und zwar komplementäre Lösungen. Eine komplementäre Lösung dieser Relation ist dann gegeben, wenn die Nebenkondition $A_1 < A_2 < A_3 < A_4 < A_5 < A_6$ und $B_1 < B_2 < B_3 < B_4 < B_5 < B_6$ und $A_1 + B_6 = A_2 + B_5 = A_3 + B_4 = A_4 + B_3 = A_5 + B_2 = A_6 + B_1$ erfüllt ist. Setzt man nun $k = \frac{A_1 + B_6}{2}$, dann gibt

$$A_1 - k,\ A_2 - k,\ \cdots,\ A_6 - k \overset{4}{=} B_1 - k,\ B_2 - k \cdots,\ B_6 - k$$

Lösungen für $\sum_{i=1}^{3} G_i^n = \sum_{i=1}^{3} J_i^n$ für $n = 1, 3$ oder Lösungen für $\sum_{i=1}^{2} K_i^n = \sum_{i=1}^{4} L_i^n$ für $n = 1, 3$ (*Cf.* A. Moessner: "Zahlentheoretische Untersuchungen" in *The Tohoku Mathematical Journal*, Vol. 39, Part 1 !).

Beispiel: Bei 4, 14, 15, 15, 25, 29 $\overset{4}{=}$ 5, 9, 19, 19, 20, 30 ergibt $k = \frac{4 + 30}{2} = 17$ das Resultat $-13, -3, -2, -2, 8, 12 \overset{4}{=} -12, -8, 2, 2, 3, 13$, also

$$\begin{cases} 8 + 12 = 2 + 2 + 3 + 13 \\ 8^3 + 12^3 = 2^3 + 2^3 + 3^3 + 13^3. \end{cases}$$

Wir befassen uns nun zunächst mit den Relationen $\sum_{i=1}^{3} G_i^n = \sum_{i=1}^{3} J_i^n$ für $n = 1, 3$ und $\sum_{i=1}^{2} K_i^n = \sum_{i=1}^{4} L_i$ für $n = 1, 3$. Dabei sollen Lösungen gegeben werden, welche bisher in der Literatur nicht gezeigt wurden und einige Spezialfälle aufgeführt werden.

(1) Bei gewissen Lösungen zu $\sum_{i=1}^{3} G_i^n = \sum_{i=1}^{3} J_i^n$ für $n = 1, 3$ lassen sich die Zahlen so vertauschen, dass das Produkt der Wurzeln der linken Gleichungsseite dem Produkte der Wurzeln der rechten Gleichungsseite gleich

ist. So ergibt $1, 12, 15 \overset{n}{=} 2, 10, 16$ für $n = 1, 3$ die Relation

$$\begin{cases} 1 + 15 + (-16) = 2 + 10 + (-12) \\ 1^3 + 15^3 + (-16)^3 = 2^3 + 10^3 + (-12)^3 \\ 1 \cdot 15 \cdot (-16) = 2 \cdot 10 \cdot (-12). \end{cases}$$

Wir bekommen Lösungen des Systems

$$\begin{cases} H_1, H_2, H_3 \overset{n}{=} Q_1, Q_2, Q_3 \text{ für } n = 1, 3 \\ H_1 \cdot H_2 \cdot H_3 = Q_1 \cdot Q_2 \cdot Q_3, \end{cases}$$

wenn wir setzen

$$\begin{aligned} H_1 &= p\,(pc^2 - qd^2); & Q_1 &= q\,(pc^2 - qd^2); \\ H_2 &= c\,(-p^2c + q^2d); & Q_2 &= d\,(-p^2c + q^2d); \\ H_3 &= qd\,(-qc + pd); & Q_3 &= cp\,(-qc + Pd); \end{aligned}$$

wobei c, d, p, q beliebig sind.

Beispiel: $c = 2, d = 1, q = 3, p = 1$ gibt das Resultat

$$\begin{cases} 1, 14, (-15) \overset{n}{=} 3, 7, (-10) & (n = 1, 3) \\ 1 \cdot 14 \cdot (-15) = 3 \cdot 7 \cdot (-10). \end{cases}$$

(2) Ich gebe nun eine allgemeine Lösung der Relation $\sum_{i=1}^{3} G_i^n = \sum_{i=1}^{3} J_i^n$ für $n = 1, 3$ in vier Parametern. Wir setzen

$$\begin{aligned} G_1 &= m^2n - mn^2 + qr\,(2n - q - r); \\ G_2 &= m^2n + m\,(n^2 - 2qr) - qr\,(2n - q - r); \\ G_3 &= -m^2n + m\,(n^2 + 2qr) - qr\,(q + r); \\ J_1 &= m^2n + m\,(n^2 - 2nr) - qr\,(q - r); \\ J_2 &= -m^2n - m\,(n^2 - 2nq - 2nr) - qr\,(q + r); \\ J_3 &= m^2n + m\,(n^2 - 2nq) + qr\,(q - r); \end{aligned}$$ wobei m, n, q, r beliebig sind.

Beispiel: $m = 5, n = 2, q = 4, r = 1$ ergibt nach Kürzung der Basen durch 2 das Resultat $13, 17, (-5) \overset{n}{=} 19, 5, 1$ für $n = 1, 3$; bei Ordnung der Glieder nach Grösse: $(-5), 13, 17 \overset{n}{=} 1, 5, 19$ für $n = 1, 3$.

(3) Wir lösen die Identität $C_1, C_2, C_3 \overset{n}{=} D_1, D_2, D_3$ für $n = 1, 3$, wo $C_3 - C_2 = C_2 - C_1$ ist, also einen Spezialfall der Identität $\sum_{i=1}^{3} G_i^n = \sum_{i=1}^{3} J_i^n$ für $n = 1, 3$. Wir setzen

$$\begin{aligned} C_1 &= -usf^2 - 3s^2fg - (u - 3s)\,(2u - 3s)\,g^2; \\ C_2 &= g\,[-s^2f + (2u^2 - 3s^2)\,g]; \\ C_3 &= usf^2 + s^2fg + 3\,(u - s)\,(2u - s)\,g^2; \\ D_1 &= -s^2f^2 - 3s^2fg + 2u\,(3u - 4s)\,g^2; \\ D_2 &= f\,[s^2f - (2u^2 - 3s^2)\,g]; \\ D_3 &= g\,[(2u^2 - 3s^2)\,f + s\,(8u - 9s)\,g]; \end{aligned}$$ wo u, s, f, g beliebig sind.

Beispiel: $u = 3$, $s = 2$, $f = 3$, $g = -2$ ergibt das Resultat 3, 8, 13 $\overset{n}{=}$ 2, 10, 12 für $n = 1, 3$.

(4) Besteht eine Identität von der Form $\sum_{i=1}^{3} C_i^n = \sum_{i=1}^{3} D_i^n$ für $n = 1, 3$, dann gilt für beliebiges t die Relation $t - C_3, t - C_2, t - C_1\ t + D_1, t + D_2, t + D_3 \overset{4}{=} t - D_3, t - D_2, t - D_1, t + C_1, t + C_2, t + C_3$ und wir bekommen so Lösungen zu $A_1, A_2, \cdots A_6 \overset{4}{=} B_1, B_2, \cdots, B_6$. Geht man von der Relation $\sum_{i=1}^{3} C_i^n = \sum_{i=1}^{3} D_i^n$ für $n = 1, 3$ aus, wo $C_3 - C_2 = C_2 - C_1$, so bekommt man Lösungen zu $A_1, A_2, \cdots, A_6 \overset{4}{=} B_1, B_2, \cdots, B_6$, welche die Wurzeldifferenz $C_3 - C_2 = C_2 - C_1$, die wir mit h bezeichnen wollen, 4 mal, bei noch an deren Konditionen 6 mal enthalten. Es ergibt $t = 14$ für 3, 8, 13 $\overset{n}{=}$ 2, 10, 12 für $n = 1, 3$ das Resultat 1, 6, 11, 16, 24, 26 $\overset{4}{=}$ 2, 4, 12, 17, 22, 27.

Setzt man bei Relationen der Form $\sum_{i=1}^{6} A_i^n = \sum_{i=1}^{6} B_i^n$ für $n = 1, 2, 3, 4$, welche die Wurzeldifferenz h 4 mal oder 6 mal enthalten, diese Differenz in der Weise $A_1, A_2 \cdots A_6, B_1 + h, B_2 + h, \cdots, B_6 + h \overset{5}{=} B_1, B_2, \cdots, B_6, A_1 + h, A_2 + h, \cdots, A_6 + h$,
dann ergeben sich nach dem binomischen Lehrsatz, da sich auf beiden Gleichungsseiten 4 oder 6 Glieder streichen lassen, Identitäten von der Form $\sum_{i=1}^{8} U_i^n = \sum_{i=1}^{8} V_i^n$ für $n = 1, 2, 3, 4, 5$ oder von der Form $\sum_{i=1}^{6} U_i^n = \sum_{i=1}^{6} V_i^n$ für $n = 1, 2, 3, 4, 5$.

Es folgt aus 1, 6, 11, 16, 24, 26 $\overset{4}{=}$ 2, 4, 12, 17, 22, 27 für $h = 5$ das Resultat 1, 7, 9, 24, 25, 32 $\overset{5}{=}$ 2, 4, 12, 21, 29, 31.

Besteht eine *komplementäre* Lösung zu $\sum_{i=1}^{z} U_i^n = \sum_{i=1}^{z} V_i^n$ für $n = 1, 2, 3, 4, 5$, so gilt für diese Lösungen, wenn $U_1 < U_2 < U_3 < \cdots < U_z$ und $V_1 < V_2 < V_3 < \cdots < V_z$, zugleich

$$(U_1 \cdot U_z),\ (U_2 \cdot U_{z-1}),\ (U_3 \cdot U_{z-2}),\ (U_4 \cdot U_{z-3}) \cdots \left(U_{\frac{z}{2}} \cdot U_{\frac{z}{2}+1}\right) \overset{2}{=}$$

$$(V_1 \cdot V_z),\ (V_2 \cdot V_{z-1}),\ (V_3 \cdot V_{z-1}),\ (V_4 \cdot V_{z-3}) \cdots \left(V_{\frac{z}{2}} \cdot V_{\frac{z}{2}+1}\right).$$

Es ergibt unser Zahlenbeispiel das Resultat

$$(1 \cdot 32),\ (7 \cdot 26),\ (9 \cdot 24) \overset{2}{=} (2 \cdot 31),\ (4 \cdot 29),\ (12 \cdot 21).$$

(5) Ich löse die Relation $\sum_{i=1}^{3} G_i^n = \sum_{i=1}^{3} J_i^n$ für $n = 1, 3$, wobei ein Glied O ist.

Dieser Spezialfall ist identisch mit der Identität $x, y \overset{n}{=} a, b, c$, für $n = 1, 3$, wofür mit

$$x = g\,[r\,(2n - r)\,f - n^2 g]\,; \qquad a = (n - r)\,(rf^2 - ng^2)\,;$$
$$y = rf\,[nf - (2n - r)\,g]\,; \qquad b = (-rf + ng)\,[(n - r)\,f - ng]\,;$$
$$c = n\,(f - g)\,[rf - (n - r)\,g]\,;$$

$-f, g, n, r$ beliebig—eine allgemeine Lösung gegeben ist.

Beispiel: $f = 2, g = 1, n = 1, r = 2$ gibt $8, 7 \overset{n}{=} 1, 5, 9$ für $n = 1, 3$.

Aus $x, y \overset{n}{=} a, b, c$ für $n = 1, 3$ folgt $x, y, -a, -b, -c \overset{4}{=} a, b, c, -x, -y$, also eine Lösung zu $E_1, E_2, \cdots, E_5 \overset{4}{=} F_1, F_2, \cdots, F_5$. Unser letztes Exempel ergibt $8, 7, -1, -5, -9 \overset{4}{=} 1, 5, 9, -8, -7$. Besteht nun eine Identität $E_1, E_2, \cdots, E_z \overset{n}{=} F_1, F_2, \cdots, F_z$ für die n ersten Potenzgrade, so gilt für beliebiges b die Relation $E_1 + b, E_2 + b, \cdots, E_z + b \overset{n}{=} F_1 + b, F_2 + b, \cdots, F_z + b$ für die gleichen n ersten Potenzgrade. Es ergibt $b = 10$ bei dem letzten numerischen Exempel $18, 17, 9, 5, 1 \overset{4}{=} 11, 15, 19, 2, 3$, also eine Lösung mit nur positiven Zahlen.

II. (1) Wir lösen $x, y, z \overset{n}{=} a, b, c$, für $n = 1, 3$ *mit der Bedingung* $x - y = a - b$.

Eine Lösung hiefür ist gegeben durch die Formel

$$[f(2\alpha - \beta) + \alpha g],\ [f2\alpha + \beta) - \alpha g],\ [f(-2\alpha + \beta) + g(\alpha + 2\beta)] \overset{n}{=}$$
$$[-\beta f + (\alpha + 2\beta)\,g],\ [\beta f - (\alpha - 2\beta)\,g],\ [f(2\alpha + \beta) + g(\alpha - 2\beta)]$$
für $n = 1, 3$.

Beispiel: $\alpha = 2, \beta = 1, f = 5, g = 4$, ergibt $23, 17, 1 \overset{n}{=} 11, 5, 25$.

(2) Eine Lösung zu $x, y, \overset{n}{=} a, b, c$ für $n = 1, 3$ $x - y = a - b$ ist gegeben durch die einfache Formel

$$[(\alpha + \beta)\,(2\alpha - \beta)],\ [\beta\,(3\alpha + \beta)] \overset{n}{=} [(\alpha - \beta)\,(\alpha + 2\beta)],\ [-\alpha\,(\alpha - 3\beta)],$$
$$[2\,(\alpha^2 + \beta^2]\ \text{für}\ n = 1, 3.$$

Beispiel: $\alpha = 2, \beta = 1$, gibt $9, 7 \overset{n}{=} 4, 2, 10$ für $n = 1, 3$.

(3) Eine Lösung zu $x, y, z \overset{n}{=} a, b, c$, für $n = 1, 3$ mit der Kondition $x - y = y - z$ und $a - b = 2\,(x - y) = 2\,(y - z)$ ist gegeben durch die Formel $[3\alpha^2 + \alpha\beta - \beta^2],\ [\alpha\,(\alpha + 2\beta)],\ [-\alpha^2 + 3\alpha\beta + \beta^2] \overset{n}{=} [(\alpha + 2\beta)$
$(2\alpha - \beta)],\ [-\alpha\,(2\alpha - 5\beta)],\ [3\alpha^2 - 3\alpha\beta + 2\beta^2]$ für $n = 1, 3$.

$\alpha = 3, \beta = 2$ gibt $29, 21, 13, \overset{n}{=} 28, 12, 23$ für $n = 1, 3$.

(4) Endlich sei der Spezialfall, dass bei $x,\ y \overset{n}{=} a,\ b,\ c$ für $n = 1,\ 3$ die Zahlen $a,\ b,\ c$ eine arithmetische Progression bilden, gelöst durch die Formel

$$[(2f - 3g)(2f + g)],\ [2\ (f - g)(f + 3g)] \overset{n}{=} [3g\,(f - 2g)],\ [2f^2 - 3g^2],$$
$$[f\,(4f - 3g)],\ \text{für } n = 1,\ 3.$$

Beispiel: $f = 4,\ g = 1$, ergibt $42,\ 45 \overset{n}{=} 6,\ 29,\ 52$ für $n = 1,\ 3$.

Die Identitat $x,\ y \overset{n}{=} a,\ b,\ c$ für $n = 1,\ 3$, wo $a,\ b,\ c$ eine arithmetische Progression bilden, führt zu einer Relation der Form $\sum_{i=1}^{5} E_i^n = \sum_{i=1}^{5} F_i^n$ für $n = 1,\ 2,\ 3,\ 4$, (*cf.* 1, 5 !), welche die Basendifferenz $c - b = b - a$ immer 4 mal enthält. Sie lässt sich daher nach der unter I, 4 gezeigten Methode immer zu einer Lösung der Identität $\sum_{i=1}^{6} U_i^n = \sum_{i=1}^{6} V_i^n$ für $n = 1, 2, 3, 4, 5$ weiterführen wenn man $h = c - b = b - a$ setzt.

Beispiel: Die gefundene Relation $42,\ 45 \overset{n}{=} 6,\ 29,\ 52$ für $n = 1,\ 3$ ergibt $8,\ 11,\ 59,\ 82,\ 105 \overset{4}{=} 1,\ 24,\ 47,\ 95,\ 98$ und daraus ergibt $h = 23$ das Resultat $8,\ 11,\ 29,\ 70,\ 118,\ 121 \overset{n}{=} 1,\ 31,\ 34,\ 95,\ 98,\ 128$ woraus nach der Theorie von simultanen Identitäten $113,\ 107,\ 11 \overset{n}{=} 127,\ 67,\ 61$ für $n = 2,\ 4$ wird.

(5) Wir gehen aus von der Identität $M_1 + M_2 + M_3 = N_1 + N_2 + N_3 = \text{Summe}_1 = S_1$, wo $M_1^2 + M_2^2 + M_3^2 = \text{Summe}_2 = S_2 \neq N_1^2 + N_2^2 + N_3^2 = S_2^1$ und $M_1^2 + M_2^3 + M_3^3 = \text{Summe}_3 = S_3 \neq N_1^2 + N_2^3 + N_3^3 = S_3^1$.

Hier können immer 5 Zahlen vorausgegeben werden. Nun bestimmen wir $K = -\dfrac{S'_3 + S_3}{3(S'_2 - S_2)}$. Dann gibt

$M^1 - K,\ M_2 - K,\ M_3 - K \overset{n}{=} N_1 - K,\ N_2 - K,\ N_3 - K$ für $n = 1,\ 3$.
Wir bekommen also auf diese eigenartige Weise Solutionen der Relation $\sum_{i=1}^{3} G_i^n = \sum_{i=1}^{3} J_i^n$ für $n = 1,\ 3$.

Beispiel: Es sei $S_1 = 2 + 3 + 5 = 0 + 4 + 6 = S_2$; dann ist $K = \dfrac{-280 + 160}{3\,(52 - 38)} = \dfrac{-20}{7}$ und, da das negative Vorzeichen unberücksichtigt bleiben kann, ergibt sich $2\,\dfrac{-20}{7},\ 3\,\dfrac{-20}{7},\ 5\,\dfrac{-20}{7} \overset{n}{=} 0\,\dfrac{-20}{7},\ 4\,\dfrac{-20}{7},\ 6\,\dfrac{-20}{7}$ für $n = 1,\ 3$; in ganzen Numbers $(-6),\ 1,\ 15 \overset{n}{=} (-20),\ 8,\ 22$ für $n = 1,\ 3$.

Bemerkung: (α) $M_1 = M_2 = M_3$, $N_1 = N_2$ führt immer auf (-1), (-1) $(-1) \overset{n}{=} (-4)$, (-4), 5 für $n = 1, 3$.

(β) $M_1 = M_2 = M_3$, $N_1 \neq N_2 \neq N_3$ führt zu einer Identität vom Typ. 3. $k^n = u^n + v^n + w^n$ für $n = 1, 3$. So führt $3 + 3 + 3 = 1 + 2 + 6$ nach Multiplikation der gefundenen Lösung mit -1 zu $3 \cdot 3^n = 17^n + 10^n + (-18)^n$ für $n = 1, 3$.

III. (1) Es sollen nun in die simultane Identität $\sum_{i=1}^{6} A_i^n = \sum_{i=1}^{6} B_i^n$ für $n = 1, 2, 3, 4$ Zahlen eingebaut werden, welche eine oder mehrere gleiche Potenzsummen aufweisen. Wir lösen zu diesem Zwecke die bezeichnete Identität nach folgender Methode. Wir gehen wieder aus von der Identität $M_1 + M_2 + M_3 = N_1 + N_2 + N_3 = S_1$, wo $S_2 \neq S_2^1$ und $S_3 \neq S_3^1$ und wo stets 5 Numbers vorausgegeben werden können. Nun aber bestimmen wir $K = \dfrac{2\,(S_3^1 - S_3)}{3\,(S_2 - S'_2)}$. Es Können hiebei zum Exempel die M_i und 2 Glieder der N_i die gleiche, jedoch eine beliebige Potenz darstellen.

Numerisches Beispielen: $2^3 + 2^3 + 2^3 = 1^3 + 1^3 + 22$ ergibt

$$K = \frac{2\,(10650 - 1536)}{3\,(192 - 486)} = -\frac{62}{3}.$$

(2) Besteht nun die Gleichung $M_1 + M_2 + M_3 = N_1 + N_2 + N_3$ mit der Kondition, dass $S_2 \neq S_2^1$ und $S_3 \neq S_3^1$, dann gilt sofort die Identität M_1, M_2, M_3, $K - N_3$, $K - N$, $\overset{4}{=} N_1 N_2 N_3$, $K - M_3$, $K - M_2$. $K - M_1$. Somit ergibt das numerische Exempel unter (1) das Resultat (das negative Vorzeichen bei $\frac{62}{-3}$ kann unberücksichtigt bleiben) 2^3, 2^3, 2^3, $\left(\frac{-4}{3}\right)$, $\frac{59}{3}$, $\frac{59}{3}$ $\overset{4}{=} 1^3$, 1^3, $\frac{38}{3}$, $\frac{38}{3}$, $\frac{38}{3}$, also in ganzen Zahlen

6^3, 6^3, 6^3, (-36), 531, 531 $\overset{4}{=} 3^3$, 3^3, 594, 342, 342, 342.

Anderes Beispielen: Aus $49 + 75 + 107 = 39 + 92 + 100$ ergibt $K = 96$ die Lösung

$$\begin{cases} (-4),\ 4,\ 57,\ 42,\ 75,\ 107 \overset{4}{=} (-11),\ 21,\ 47,\ 39,\ 92,\ 100, \text{ (Zahlen nach Grösse geordnet).} \\ (-4) + 4 + 57 = (-11) + 21 + 47 \\ 49 + 75 + 107 = 39 + 92 + 100 \\ 49^5 + 75^5 + 107^5 = 39^5 + 92^5 + 100^5. \end{cases}$$

Mit gleicher Methode lösen wir die Gleichungen

$$\begin{cases} f_1 + f_2 + f_3 + 49^5 + 75^5 + 107^5 = g_1 + g_2 + g_3 + 39^5 + 92^5 + 100^5 \\ f_1^2 + f_2^2 + f_3^2 + 49^{10} + 75^{10} + 107^{10} = g_1^2 + g_2^2 + g_3^2 + 39^{10} + 92^{10} + 100^{10} \\ f_1^3 + f_2^3 + f_3^3 + 49^{15} + 75^{15} + 107^{15} = g_1^3 + g_2^3 + g_3^3 + 39^{15} + 92^{15} + 100^{15} \\ f_1^4 + f_2^4 + f_3^4 + 49^{20} + 75^{20} + 107^{20} = g_1^4 + g_2^4 + g_3^4 + 39^{20} + 92^{20} + 100^{20}, \end{cases}$$

überhaupt allgemein $f_1, f_2, f_3, U^5, V^5, W^5 \overset{4}{=} g_1, g_2, g_3, X^5, Y^5, Z^5$, indem wir die vorher berechneten Zahlen $U^5, V^5, W^5, X^5, Y^5, Z^5$ vorausgeben.

Bemerkung: Eine allgemeine Lösung der Relation $U^5 + V^5 + W^5 = X^5 + Y^5 + Z^5$ gab ich in "Wiskundige Opgaven met de Oplossingen" 1039, page 185*). Die f_i und g_i lassen sich sodann berechnen.

(3) Aus vorstehenden Ausführungen ergibt sich durch simple Ueberlegungen,

(α) dass die Relation $C_1^v, C_2^v, D_3^v, D_1, D_2, D_3 \overset{4}{=} E_1^v, E_2^v, E_3, E_1, F_2, F_3$ für beliebiges v in ganzen Zahlen lösbar ist,

(β) dass sich in die Identität $\sum_{i=1}^{6} A_i^n = \sum_{i=1}^{6} B_i^n$ für $n = 1, 2, 3, 4$ eine Reihe von Identitäten einbauen lässt die hier nicht einzeln aufgeführt werden sollen.

Zwei numersiche Exempel sollen hier noch gezeigt werden.

Wir bauen die Relation $\begin{cases} 7^2 + 7^2 = 3^2 + 5^2 + 8^2 \\ 7^4 + 7^4 = 3^4 + 5^4 + 8^4 \end{cases}$ ein.

[Ueber die Lösung der Relation $a, a \overset{n}{=} b, c, d$ für $n = 2, 4$ *see* A. Moessner: "Numerische Identitäten" in *Boletin Matematico*, 1934, 7; und A. Moessner: "On the Equation $A_1^n + A_2^n + \cdots + A_z^n = B_1^n + B_2^n + \cdots + B_z^n$ ($n = 1, 2, 3, 4, 5, 6$) and allied Forms" in *The Mathematics Student*, 1934, 3 (Madras) !]

Wir bestimmen aus $x + 7 + 7 = 3 + 5 + 8$ die Zahl K. Es sei $x = 2$, dann ist $K = -5$. Wir setzen dafür (weil hier zulässig) 5 und bekommen die Solution

$$\begin{cases} 2, 7, 7, 2, 0, (-3) \overset{4}{=} 3, 5, 8, 3, (-2), (-2) \\ 7^2 + 7^2 = 3^2 + 5^2 + 8^2 \\ 7^4 + 7^4 = 3^4 + 5^4 + 8^4 \end{cases}$$

Aus $3^3 + 4^3 + 5^3 = 0 + 0 + 6^3$ folgt $K = \frac{2614248}{13103}$ und somit das Resultat

$$\underline{3^3}, \underline{4^3}, \underline{5^3}, \frac{2614248}{13103}, \frac{2614248}{13103}, \frac{(-216000)}{13103} \overset{4}{=} \underline{6^3}, \frac{976373}{13103}, \frac{1775656}{13103}, \frac{2260467}{13103},$$

welches bei Multiplikation der Basen mit 13103 ganzzahlig wird. Die unterstrichenen Zahlen bedeuten die Ausgangsrelation. Eine Lösung der Identität $G_1^v, G_2^v, G_3^v H, H, J \overset{4}{=} L^v, Q_1, Q_2, Q_3$ für $v > 3$ scheint mit rationalen Zahlen unmöglich zu sein.

(4) Wir gehen aus von der Identität $P_1, P_2, P_3, P_4 \overset{3}{=} Q_1, Q_2, Q_3, Q_4$, zu welcher wir nichtkomplementäre Lösungen suchen nach der Formel

$(4x^2 - 3xy + 32y^2)$, $(-2x^2 - 15xy - 16y^2)$, $(2x^2 + 9xy - 32y^2)$,
$(4x^2 + 9xy + 16y^2) \overset{3}{=} (-4x^2 - 3xy - 32y^2)$, $(2x^2 - 15xy + 16y^2)$,
$(4x^2 + 9xy - 16y^2)$, $(-2x^2 + 9xy + 32y^2)$.

Beispiel: $x = 8$, $y = 5$ gibt 39, (-47), (-13), $21 \overset{3}{=} (-49)$, (-3), 9, 43. Es ergibt $b = 50$ (*cf.* I, 5 !) bei gleichzeitiger Ordnung der Zahlen nach Grösse 3, 37, 71, 89 $\overset{3}{=}$ 1, 47, 59, 93, daraus $\frac{3+1}{2}$, $\frac{37+1}{2}$, $\frac{71+1}{2}$, $\frac{89+1}{2} \overset{3}{=} \frac{1+1}{2}$, $\frac{47+1}{2}$, $\frac{59+1}{2}$, $\frac{93+1}{2}$, also 2, 19, 36, 45 $\overset{3}{=}$ 1, 24, 30, 47.

Bemerkung: Setzt man bei dem gefundenen Exempel $h = 17$ (*cf.* I, 4 !) dann bekommt man 2, 18, 41, 45, 64 $\overset{4}{=}$ 1, 24, 30, 53, 62, mit nichtkomplementären Nombres. Aus dieser Solution ergibt $h = 23$ das Resultat 2, 18, 45, 47, 76, 85 $\overset{5}{=}$ 1, 25, 30, 62, 68, 87. Ich kenne nur diese einzige *nicht*komplementäre Solution zur Identität $\sum_{i=1}^{6} U_i^n = \sum_{i=1}^{6} V_i^n$ für $n = 1, 2, 3, 4, 5$. Besteht die Identität $\sum_{i=1}^{6} U_i^n = \sum_{i=1}^{6} V_i^n$ für $n = 1, 2, 3, 4, 5$ und setzt man $s = \frac{1}{6}(U_1 + U_2 + U_3 + \cdots + U_6)$, dann gibt $U_1 - s$, $U_2 - s$, $U_3 - s$, $\cdots U_6 - s \overset{n}{=} V_1 - s$, $V_2 - s$, $V_3 - s$, $\cdots$, $V_6 - s$ eine Relation von der Form $\sum_{i=1}^{6} X_i^n = \sum_{i=1}^{6} Y_i^n$ für $n = 1, 2, 3, 4, 5, 7$. Unser gefundenes Exempel führt, wenn man die Wurzeln mit 2 multipliziert, zu 4, 36, 90, 94, 152, 170 $\overset{5}{=}$ 2, 50, 60, 124, 136, 174 und $s = \frac{1}{6}(4 + 36 + \cdots + 170) = 91$ ergibt (-87), (-55), (-1), 3, 61, 79 $\overset{n}{=} (-89)$, (-41) (-31), 33, 45, 83 für $n = 1, 2, 3, 4, 5, 7$.

(5) Besteht die Identität P_1, P_2, P_3, $P_4 \overset{3}{=} Q_1$, Q_2, Q_3, Q_4 und setzt man $s = \frac{1}{4}(P_1 + P_2 + P_3 + P_4)$, dann gilt $(P_1 - s)$, $(P_2 - s)$, $(P_3 - s)$, $(P_4 - s) \overset{n}{=} (Q_1 - s)$, $(Q_2 - s)$, $(Q_3 - s)$, $(Q_4 - s)$ für $n = 1, 2, 3, 5$, wobei die Summe der Basen 0 beträgt, also eine Identität der Form $\sum_{i=1}^{4} W_i^n = \sum_{i=1}^{4} Z_i^n$ für $n = 1, 2, 3, 5$.

Beispiel: Multipliziert man die Wurzeln von 2, 19, 36, 45 $\overset{3}{=}$ 1, 24, 30, 47, um ganze Zahlen zu bekommen, mit 2, so bekommt man 4, 38, 72, 90 $\overset{3}{=}$ 2, 48, 60, 94 und daraus $s = \frac{1}{4}(4 + 38 + 72 + 90) = 51$, so bekommt man (-47), (-13), 21, 39 $\overset{n}{=} (-49)$, (-3), 9, 43.

(6) Gilt $\sum_{i=1}^{4} W_i^n = \sum_{i=1}^{4} Z_i^n$ für $n = 1, 2, 3, 5$, dann gilt auch

$$\begin{cases} (W_1 + W_2)^2 + (W_1 + W_3)^2 + W_1 + W_4)^2 = (Z_1 + Z_2)^2 + (Z_1 + Z_3)^2 \\ \qquad\qquad + (Z_1 + Z_4)^2 \\ (W_1 + W_2) \cdot (W_1 + W_3) \cdot (W_1 + W_4) = (Z_1 + Z_2) \cdot (Z_1 + Z_3) \cdot (Z_1 + Z_4) \end{cases}$$

Unser numerische Exempel führt zu dem Resultat

$$\begin{cases} (-47 - 13)^2 + (-47 + 21)^2 + (-47 + 39)^2 = \\ \qquad\qquad (-49 - 3)^2 + (-49 + 9)^2 + (-49 + 43)^2 \\ (-47 + 13) \cdot (-47 + 21) \cdot (-47 + 39) = \\ \qquad\qquad (-49 - 3) + (-49 + 9) + (-49 + 43). \end{cases}$$

IV. (1) Wir lösen die Relation $\sum_{i=1}^{6} A_i^n = \sum_{i=1}^{6} B_i^n$ für $n = 1, 2, 3, 4$ mit folgender Methode. Wir gehen aus von dem Theorem: Gilt die Relation

$$\begin{cases} X_1 + X_2 + X_3 = Y_1 + Y_2 + Y_3 \\ X_1 \cdot X_2 \cdot X_3 = Y_1 \cdot Y_2 \cdot Y_3 \end{cases}$$ und ist $s = X_1 + X_2 + X_3$, dann gilt auch die Identität

$$X_1, X_2, X_3, s - Y_3, s - Y_2, s - Y_1 \overset{4}{=} Y_1, Y_2, Y_3, s - X_3, s - X_2, s - X_1$$

womit $\sum_{i=1}^{6} A_i^n = \sum_{i=1}^{6} B_i^n$ für $n = 1, 2, 3, 4$ gelöst ist.

Eine solution für

$$\begin{cases} X_1 + X_2 + X_3 = Y_1 + Y_2 + Y_3 \\ X_1 \cdot X_2 \cdot X_3 = Y_1 \cdot Y_2 \cdot Y_3 \end{cases}$$ ist gegeben, wenn wir setzen

$X_1 = (ab - cd)\, a$; $X_2 = (ab - cd)\, b$; $X_3 = (a + b - c - d)\, cd$; $Y_1 = (ab - cd)\, c$; $Y_2 = (ab - cd)\, d$; $Y_3 = (a + b - c - d)\, ab$

Beispiel: $a = b = r$, $c = 4$, $d = 1$, gibt $\begin{cases} 15 + 15 + 4 = 20 + 5 + 9 \\ 15 \cdot 15 \cdot 4 = 20 \cdot 5 \cdot 9; \end{cases}$

$s = 34$ und wir bekommen $15, 15, 4, 14, 29, 25 \overset{4}{=} 20, 5, 9, 19, 19, 30$.

(2) In diesem Zusammenhange sei auf die Relation

$$\begin{cases} X_1 + X_2 + X_3 = Y_1 + Y_2 + Y_3 = x^2 \\ X_1 \cdot X_2 \cdot X_3 = Y_1 \cdot Y_2 \cdot Y_3 = K = S^2 \end{cases}$$ hingewiesen, wofür eine einfache Solution gegeben ist, wenn wir setzen

$X_1 = 1$, $X_2 = X_3 = pq$; $Y_1 = Y_2 = p$; $Y_3 = q^2$; $n = pq$ und $2p = q + 1$

$K = 1 + q + q^2$.

$K = 1 + q + q^2$ löst man auf folgende Weise: Ist a, $a \overset{n}{=} b, c, (b + c)$ für $n = 2, 4$ gelöst (*cf.* III, 3 !), wo $c > b$, dann gibt $\frac{c}{b} = q$ eine rationale Solution zu $K = 1 + q + q^2 = S^2$.

Beispiel: $7, 7 \overset{n}{=} 3, 5, (3 + 5)$ für $n + 2, 4$ gibt $q = \frac{5}{3}$ und führt zu $1 + \frac{5}{3} = (\frac{5}{3})^2 = (\frac{7}{3})^2$.

Wir finden also folgende elementare Lösung für

$$\begin{cases} X_1 + X_2 + X_3 = Y_1 + Y_2 + Y_3 = x^2 \\ X_1 \cdot X_2 \cdot X_3 = Y_1 \cdot Y_2 \cdot Y_3 = K = S^2 \end{cases}$$

$X_1 = 1$; $X_2 = \frac{40}{9(r^2+1)}$; $X_3 = \frac{40r^2}{9(r^2+1)}$; $x = \frac{40r}{9(r^2+1)}$; $Y_1 = \frac{8}{3(r^2+1)}$;

$Y_2 = \frac{8r^2}{3(r_1+1)}$; $Y_3 = \frac{25}{9}$; $S = \frac{7}{3}$. Hier ist r beliebig.

$r = 1$ gibt, auf ganzen Zahlen gebracht, das Resultat

$$\begin{cases} 9 + 20 + 20 = 12 + 12 + 25 = 7^2 \\ 9 \cdot 20 \cdot 20 = 12 \cdot 12 \cdot 25 = 60^2. \end{cases}$$

(3) Die Relation unter (2) führt nach der unter (1) gezeigten Methode zu Identitäten vonder Form X_1, X_2, X_3, A, B, $B \overset{4}{=} Y$, Y_2, Y_3, C, C, D, wo $\text{Summe}_1 = S_1 = 3 \cdot S^2$.

Das Exempel unter (2) führt zu dem Resultat 9, 20, 20, 24, 37, $37 \overset{4}{=}$ 12, 12, 25, 29, 40, wo $S = 3 \cdot 7^2$.

(4) Wir lösen das System

$$\begin{cases} E^2 + F^4 + F^4 + G^2 = H_1 + H_2 + H_3 + H_4 \\ E^4 + F^8 + F^8 + G^4 = H_1^2 + H_2^2 + H_3^2 + H_1^2 \\ E^6 + F^{12} + F_1^2 + G^6 = H_1^3 + H_2^3 + H_3^3 + H_4^3 \end{cases}$$

in ganzen Numbers.

Besteht die pythagoräische Gleichung $a^2 = b^2 + c^2$, dann besteht zugleich die Relation $2a^2 = (c-b)^2 + (b+c)^2$ und es bilden $(c-b)^3$, a^2, $(b+c)^2$ eine arithmetische Progression mit der Differenz $2bc$. Bildet man nun die Gleichung $0^2 + (2bc)^2 = \left(\frac{2bc \cdot b}{a}\right)^2 + \left(\frac{2bc \cdot c}{a}\right)^2$ und setzt man $T = a^2$, dann gibt $(T - 2bc)$, $(T - 0)$, $(T + 0)$ $(T + 2bc \overset{3}{=} \left(T - \frac{2bc \cdot c}{a}\right)$, $\left(T + \frac{2bc \cdot b}{a}\right)$, $\left(T + \frac{2bc \cdot b}{a}\right)$, $\left(T + \frac{2bc \cdot c}{a}\right)$, auf ganze Numbers gebracht, Solutionen des vorgelegter Systems.

Beispiel: $5^2 = 3^2 + 4^2$ führt zu $0^2 + 24^2 = \left(\frac{24 \cdot 3}{5}\right)^2 + \left(\frac{24 \cdot 4}{5}\right)^2$; $T = 5^2 = 25$ ergibt 1, 25, 25, $49 \overset{3}{=} \frac{29}{5}, \frac{53}{5}, \frac{197}{5}, \frac{221}{5}$; auf ganze Zahlen gebracht 5^2, 5^4, 5^4, $35^2 \overset{3}{=}$ 145, 265, 985, 1105.

(5) Zum Schlusse sei eine Lösung zu $Q_1, Q_2, \ldots Q_7 \overset{n}{=} R_1, R_2, \ldots R_7$ für $n = 2, 4, 6, 8, 10$ entwickelt. Eine Lösung dieser Identität wurde bisher in der Literatur nicht gegeben.

Wir gehen aus von der Relation 1, 15, 17, 31, 42, 47, 54 $\overset{n}{=}$ 3, 9, 21, 34, 37, 50, 53, für $n = 2, 4, 6, 8$. Wir setzen $T = 55$ [*cf.* (4) !]. Hier kann T beliebig sein, aber wir wählen es so, dass wir möglichst kleine und doch posttive Zahlen bekommen. $T = 55$ ergibt

1, 18, 13, 24, 38, 40, 54, 56, 70, 72, 86, 97, 102, 109 $\overset{9}{=}$ 2, 3, 18, 21, 34, 46, 52, 58, 64, 76, 89, 92, 105, 108.

Setzt man hier $h = 16$ (*cf.* I, 4 !), so ergibt sich nach der Theorie von den simultanen Identitäten die Relation

1, 8, 13, 37, 38, 50, 62, 68, 74, 80, 97, 109, 121, 124 $\overset{10}{=}$ 2, 5, 17, 29, 46, 52, 58, 64, 76, 88, 89, 113, 118, 125.

Daraus gibt $h = 12$ die Identität

1, 8, 14, 37, 38, 41, 68, 70, 97, 100, 101, 124, 130, 137 $\overset{11}{=}$ 2, 5, 20, 25, 46, 49, 52, 86, 89, 92, 113, 118, 133, 136. Hier ist die Konstante $K = 138$, gegeben. Es ergibt $\frac{K}{2} = 69$ (*cf.* A. Moessner: "Zahlentheoretische Untersuchunen" in *The Math. Journ. Vol.* 39, *Part* I ! das Resultat

68, 61, 55, 32, 31, 28, 1 $\overset{n}{=}$ 67, 64, 49, 44, 23, 20, 17, für $n = 2, 4, 6, 8, 10$

Eine Allgemeinelösung zu $Q_1, Q_2, \cdots, Q_7 \overset{n}{=} R_1, R_2, \cdots, R_7$ für $n = 2, 4, 6, 8, 10$, ist noch mir unbekannt.

Note by S. Chowla.—

In Hardy and Wright's "Introduction to the Theory of Numbers" (p. 333) it is mentioned that no solution in positive integers of the equation. (1) $x_1^5 + x_2^5 + x_3^5 = y_1^5 + y_2^5 + y_3^5$ is known The reader will notice that the author has solved the joint equations (1) and (2)

$$x_1 + x_2 + x_3 = y_1 + y_2 + y_3$$

with $x_1 = 49$, $x_2 = 75$, $x_3 = 107$; $y_1 = 39$, $y_2 = 92$, $y_3 = 100$.

RAMAN EFFECT AND CHEMICAL CONSTITUTION

Influence of Constitutive and other factors on the double bonds in Organic Compounds

Part II. Effect of the Phenyl Group on the Carbonyl Bond in Esters

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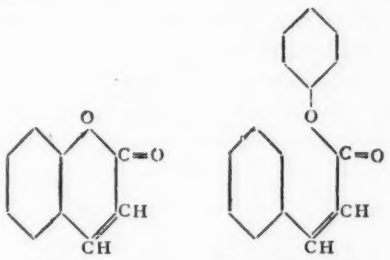
It was pointed out in the first paper[1] of this series that the large amount of existing data on the Raman spectra of organic compounds indicate considerable variations in the C = O and the C = C frequencies corresponding in a general way to the well-known differences in the chemical behaviour of these groups in different situations. From a careful scrutiny of the double bond frequencies we feel convinced that differences which do not exceed twenty wave numbers are more reliable if the various substances that are compared have been studied by the same authors under the same conditions. Further, in the early days of the study of the Raman Effect, workers seem to have been looking rather more for the general agreement in the frequencies attributable to the same linkage than to small and yet significant differences arising as a result of constitutive and other influences. We have therefore found it necessary to revise earlier work in a number of cases under standard conditions before drawing definite conclusions.

While studying the Raman spectra of the esters of cinnamic acid it was noted[2] that phenyl cinnamate exhibited a close resemblance to coumarin. This could be explained as due to the similarities in constitution as shown below :—



Coumarin I

Phenyl cinnamate II

In both of these a phenyl group is attached to the oxygen of the (COO) group. It does not obviously matter whether the same phenyl group which bears the side chain is involved as in (I) or a second phenyl group comes in for the purpose as in (II). The enhancement of the C = O frequency in coumarin therefore found a rational explanation. As a result of this a detailed examination of the influence of the phenyl group on the carbonyl frequency in esters has now been made. Raman spectra of phenyl benzoate and phenyl cinnamate have been studied in detail and compared with those of the corresponding alkyl esters. In this connection previous work on the Raman spectra of methyl and ethyl esters of benzoic and cinnamic acids has been revised. Further the spectrum of phenyl acetate has been exhaustively investigated and many lines which were not recorded before have been now found to be present.

In our studies of the double bonds we have always employed the 4358 Å.U. line of the mercury arc as the exciting source and a solution of sodium nitrite as a filter to cut off the 4046 Å.U. line. For the sake of uniformity in the results the following procedure was adopted for measuring the wave numbers of the C = O lines which are as a rule broader than most others. Where the lines were not broad the measurements were made on the micrometer scale when the crosswire coincided with the centre of the line. In case a line was broad, readings were taken at both the extremes and the average recorded as the centre of the line. For diffuse lines with non-uniform darkening on the negative the microphotometric records were always taken and the wave numbers were calculated from the distances of the peaks of the various frequencies by the application of Hartmann's dispersion formula. Each plate was measured at least twice to ensure accuracy of measurements. The same slit width was employed in all cases. The esters that were studied were mostly pure samples from Kahlbaum which were subjected to a redistillation. Phenyl cinnamate was prepared by the action of phenol on cinnamoyl chloride in the presence of pyridine. It was recrystallised several times from alcohol. Phenyl benzoate was repeatedly recrystallised from carbon tetrachloride till pure colourless crystals were obtained. Both phenyl cinnamate and phenyl benzoate were employed in carbon tetrachloride solution for obtaining the Raman spectrum whereas the others which are liquids were used as such.

TABLE I

Esters of Benzoic Acid.

Phenyl Benzoate. (Murty and Seshadri.)	Ethyl Benzoate. (Murty and Seshadri.)	Ethyl Benzoate. (Kohlrasuch and Pongratz.[3])	Methyl Benzoate. (Murty and Seshadri.)	Methyl Benzoate. (Kohlrausch and Pongratz.)
..	193 (3)	188 (6 b)	190 (3)	168 (3)
..	214 (2)	279 (1)	216 (2)	216 (5 b)
340 (3)	326 (4)	328 (5)	329 (4)	354 (5)
..	395 (1)	..	390 (1)	..
..	488 (1)	..	490 (1)	..
..	558 (1)	..	560 (1)	..
610 (3)	619 (6)	616 (6)	617 (6)	615 (6)
674 (1)	677 (4)	672 (3)	674 (3)	674 (3)
..	783 (2)	786 (2)	780 (2)	714 (1 b)
..	809 (2)	806 (2)	806 (2)	818 (8)
850 (2)	852 (5)	848 (6)	854 (5)	967 (2)
1000 (10)	1004 (10)	1001 (12)	1003 (10)	1001 (15)
1030 (2)	1029 (3)	1026 (4)	1029 (3)	1025 (4)
1115 (2)	1112 (3)	1106 (4)	1114 (3)	1108 (5 b)
1158 (2)	1160 (2)	1162 (4 b)	1158 (2)	1160 (5)
1176 (1)	1178 (2)	..	1176 (2)	1183 (4)
1274 (3)	1277 (5)	1273 (8)	1274 (5)	1276 (8 b)
1310 (1)	1314 (2)	1309 (1)	1310 (1)	1314 (2)
1365 (1)	1371 (2)	1370 (2)	1370 (2)	..
..	1391 (2)	1390 (2)	1390 (1)	..
1450 (2)	1453 (3)	1450 (3)	1450 (3)	1451 (3 b)
..	1493 (1)	1492 (1)	1493 (1)	..
1604 (10)	1602 (10)	1599 (10)	1602 (10)	1598 (14)
1740 (7)	1720 (8)	1714 ± 9 (8 b)	1720 (8)	1717 ± 8½ (10 b)
2930 (1)	2935 (2)	2931 (2 b)	2932 (2)	2954 (4 b)
..	2972 (2)	2975 (3 b)	2970 (2)	..
3070 (5)	3076 (6)	3071 (6 b)	3074 (6)	3071 (8 b)

TABLE II

Esters of Cinnamic Acid

Phenyl cinnamate. (Murty and Seshadri.)	Ethyl cinnamate. (Murty and Seshadri.)	Ethyl cinnamate. (Kohlrausch and Pongratz.[4])	Methyl cinnamate. (Murty and Seshadri.)	Methyl cinnamate. (Kohlrausch and Pongratz.)
..	..	..	..	217 (4 b)
274 (1)	270 (1)	..	270 (1)	274 (1)
357 (1)	357 (1)	..	355 (1)	357 (1)
..	..	..	..	402 (1)
580 (1)	582 (1)	582 (1)	580 (1)	576 (3)
618 (1)	619 (2)	616 (3)	617 (3)	616 (6)
715 (2)	713 (2)	718 (2)	713 (2)	710 (6)
840 (2)	836 (1)	846 (2)	833 (1)	837 (4)
945 (2)	943 (2)	..	945 (2)	938 (3)
974 (2)	972 (2)	..	970 (2)	977 (3)
1000 (7)	999 (7)	1004 (10)	998 (7)	998 (10)
1030 (3)	1030 (2)	1030 (2)	1029 (2)	1028 (1)
1153 (2)	1160 (2)	1163 (3)	1159 (2)	1165 (4)
1180 (4)	1182 (5)	1185 (10)	1183 (5)	1181 (8)
1202 (6)	1204 (6)	1201 (12)	1204 (5)	1201 (5)
1255 (2)	1250 (2)	1264 (4 b)	1250 (2)	1268 (3)
1301 (1)	1305 (1)	1303 (3)	1305 (1)	..
1450 (2)	1450 (2)	1446 (4)	1448 (2)	1447 (5)
..	1516 (1)	..	1516 (1)	..
1540 (2)	1540 (2)	..	1540 (2)	..
1570 (2)	1578 (2)	..	1576 (2)	1578 (6)
1596 (7)	1598 (7)	1595 (15 b)	1598 (7)	1598 (14)
1633 (10)	1634 (10)	1631 (20 b)	1634 (10)	1634 (20 b)
1742 (4)	1712 (5 b)	$1706 \pm 7\frac{1}{2}$ (6 b)	1710 (6 b)	$1712 \pm 10 \cdot 5$ (9b)
..	..	..	..	2836 (6)
..	..	..	..	2880 (1)
2940 (1)	2940 (1)	2934 (1)	2938 (1)	2956 (5)
..	..	2980 (1 b)	..	..
3067 (1)	3066 (1)	3053 (?)	3067 (1)	3077 (5 b)

TABLE III

Raman Spectrum of Phenyl Acetate.

Phenyl acetate. (Murty and Seshadri.)	Phenyl acetate. (Matsuno and Han.[5])	*Ethyl[6] acetate. (Landolt-Bornstein.)	Phenyl acetate. (Murty and Seshadri.)	Phenyl acetate. (Matsuno and Han.[5])	Ethyl[6] acetate. (Landolt-Bornstein.)
185 (1)	181 (3)	..	1079 (1)	..	1110 (3)
239 (4)	..	..	1163 (6)	1159 (7 b)	..
272 (4)	262 (5)	..	1195 (6)	1193 (4 br)	..
341 (1)	336 (5)	379 (5)	1262 (1)	..	..
529 (5)	525 (4)	..	1311 (1)	..	..
597 (1)	..	..	1369 (1)	1358 ($\frac{1}{2}$)	1393 (0)
618 (4)	612 (4)	..	1429 (1)	..	..
664 (4)	661 (3)	634 (6)	1448 (1)	..	1448 (5 br)
694 (2)	..	..	..	1487 (2)	..
744 (5)	746 (5)	786 (2)	1596 (8)	1590 (5)	..
815 (5)	810 (5)	..	1766 (3)	1760 (2)	1735±9 (3 br)
829 (1)	..	848 (4)	2912 (3)	2928 (7 br)	2880 (3 br) 2936 (3 br)
892 (2)	890 ($\frac{1}{2}$ b)	..	3047 (2)	..	2972 (10 br)
926 (1)	..	924 (4)	3070 (7)	3068 (8 br)	..
1004 (10)	1001 (8)	1000 (2)	..	..	..
1027 (3)	1018	1045 (2)	..	..	..

* The Raman Spectrum of ethyl acetate was studied by various workers prior to 1938 and the references are given at the end of the paper. Since their values are embodied in Landolt-Bornstein tables we have quoted above from these tables.

Discussion of the Results

1. The results obtained by us for methyl and ethyl benzoates agree closely with those of Kohlrausch and Pongratz. However it may be noted that Raman lines corresponding to 184, 780, 852, 1370 and 1390 cm.$^{-1}$ which were recorded by Kohlrausch and co-workers for ethyl benzoate and not for methyl benzoate have now been found for both. New lines 395, 488 and 588 cm.$^{-1}$ are recorded by us for both the esters. The data for the spectrum of phenyl benzoate may not be quite complete owing to the fact that there was some continuous spectrum and consequently weak lines might have escaped notice. However the phenyl ester exhibits a close

resemblance to the alkyl esters of benzoic acid except for the noteworthy difference in the frequency attributable to the C = O linkage which is 20 wave numbers higher in the phenyl ester (1740 cm.$^{-1}$) than in the methyl and ethyl esters (1720 cm.$^{-1}$).

2. Regarding the esters of cinnamic acid (Table II) the following remarks may be made.

(*a*) $\Delta\nu$ 217, 402, 2836, 2880 cm.$^{-1}$ recorded by Kohlrausch and Pongratz for methyl cinnamate was not found by them for ethyl cinnamate. Similarly the line 2980 cm.$^{-1}$ was recorded by them for ethyl cinnamate and not for the other ester. We do not get these lines in all the three esters examined.

(*b*) $\Delta\nu$ 274, 357, 938, 970 and 1578 cm.$^{-1}$ were recorded by Kohlrausch and Pongratz for methyl cinnamate and not for the ethyl ester. They have now been found to be present in all the three esters.

(*c*) $\Delta\nu$ 1516 cm.$^{-1}$ is recorded by us for the methyl and ethyl esters and $\Delta\nu$ 1540 cm.$^{-1}$ for all the three esters. These were not obtained by earlier workers.

(*d*) Our results show that there exists a greater resemblance in the Raman spectra of the esters of cinnamic acid than indicated by previous records. The phenyl ester exhibits a higher frequency for the C = O linkage (1742 cm.$^{-1}$) than the corresponding alkyl esters (1712 cm.$^{-1}$) the difference being in this case 30 wave numbers.

3. Our study of the Raman spectrum of phenyl acetate (Table III) is more exhaustive than that of Matsuno and Han. The following new frequencies have been noted now : $\Delta\nu$ 239, 597, 694, 829, 926, 1079, 1262, 1311, 1429, 1448 and 3047 cm.$^{-1}$. We feel that the Raman line 1487 cm.$^{-1}$ recorded by the previous workers is probably not a genuine line. There is no doubt a line which may be said to correspond to 1487 cm.$^{-1}$ from 4358 Å.U. But we feel that it is only the 1590 cm.$^{-1}$ line excited by the 4339 Å.U. line of the mercury arc. This view is supported by the fact that the 1590 cm.$^{-1}$ line corresponding to the component 4347 Å.U. is also excited.

The C = O frequency of phenyl acetate (1766 cm.$^{-1}$) is again higher by about 30 wave numbers than the corresponding frequency for ethyl acetate (1735 cm.$^{-1}$). This value for the alkyl ester given in the literature has been verified by us.

4. In Table IV are collected the C = O frequencies of important alkyl and phenyl esters. Phenyl (including tolyl) esters invariably exhibit higher frequencies in all the cases.

TABLE IV

Name of the ester	C=O frequency cm.$^{-1}$	Name of the ester	C = O frequency cm.$^{-1}$
(I) Methyl acetate ..	1738	(III) Methyl benzoate ..	1720
Ethyl acetate ..	1735	Ethyl benzoate ..	1720
Butyl acetate ..	1738	Propyl benzoate ..	1721
Propyl acetate ..	1739	Butyl benzoate ..	1722
Amyl acetate ..	1736	Octyl benzoate ..	1717
Allyl acetate ..	1742	Phenyl benzoate ..	1740
Phenyl acetate ..	1766	(IV) Methyl salicylate ..	1670
Tolyl acetate ..	1764	Ethyl salicylate ..	1670
(II) Methyl butyrate	1734	Phenyl salicylate ..	1693
Ethyl butyrate ..	1731	(V) Methyl cinnamate ..	1710
Phenyl butyrate	1753	Ethyl cinnamate ..	1712
		Phenyl cinnamate ..	1740

One other feature that is brought out by the above table is that esters of benzoic acid exhibit a lower frequency for the C = O groups than the corresponding esters of aliphatic acids. The abnormal lowering noticed in the case of the esters of salicylic acid is obviously due to the effect of chelation which is known to exist in these compounds. That a phenyl group attached to the carbon of the C = O group directly lowers the carbonyl frequency is also supported by the data collected in Table V relating to the other types of Carbonyl compounds.

TABLE V

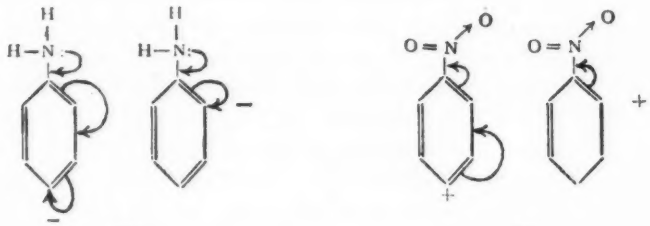
Name of the compound.	C=O frequency cm.$^{-1}$	Name of the compound.	C=O frequency cm.$^{-1}$
Acetone ..	1712	Acetaldehyde ..	1716
*Methyl ethyl ketone ..	1712	Benzaldehyde ..	1700
Acetophenone ..	1679	Acetyl chloride ..	1798
Benzophenone ..	1652	Benzoyl chloride ..	1770

* Whitelaw [*Phys. Rev.*, 1929, **34**, 376] reports 1734 for the C = O frequency in methyl ethyl ketone but we repeated the study of the substance and have found that the C = O frequency is exactly identical with that in acetone.

It is clear therefore that a phenyl group attached to the C = O through an oxygen atom as in phenyl esters markedly enhances the frequency of the group whereas the same phenyl group attached directly to the C = O as in esters of aromatic acids or as in aromatic ketones produces the opposite effect. Both these effects are very well brought out in the series methyl acetate, methyl benzoate, phenyl acetate and phenyl benzoate.

$CH_3-C-OCH_3$	$C_6H_5-C-OCH_3$	$CH_3-C-OC_6H_5$	$C_6H_5-C-OC_6H_5$
‖	‖	‖	‖
O	O	O	O
1738	1720	1766	1740

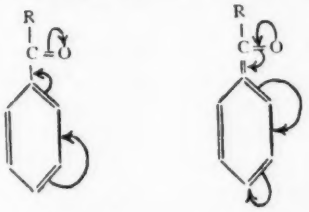
Since an increase in the carbonyl frequency indicates increased strength of the carbonyl double bond and a decrease in the frequency a weakening, it can be concluded that a phenyl group attached directly to C = O group weakens it, whereas the same attached through the oxygen atom as in phenyl esters strengthens it. It is known that unsaturated radicals like vinyl and phenyl are generally electro-positive in character leading to withdrawal of electrons towards them. However owing to the flexibility of their structures and the powers of co-operation in electromeric displacements which they can display they can also behave as negative groups tending to produce electron pressure. The different orienting and activating effect of substituent groups on the benzene ring thus finds easy explanation as below :



III IV

Wherever electromeric polarisation of type III is possible the nuclear positions are activated and *o*, *p* substitution takes place. In type IV deactivation of the nucleus and meta orientation result. A carbonyl group attached to the phenyl nucleus is known to reduce its activity and produce meta orientation. One may therefore expect a flow of electrons towards the C = O group leading to increase in the bond strength (V). But actually there is mesomerism or resonance, electromeric polarisation in the manner (VI) being also possible. As a result of this all the double bonds, including

the C = O get weakened and there exist reduced nuclear reactivity, *m* – substitution and weakening of the C = O bond.



V VI

The part played by the phenyl group in the phenyl esters is different. In alkyl esters there is only one way in which electromeric effect can play (VII). In the case of phenyl esters two modes of polarisation are possible, the first reinforcing the flow of electrons towards the carbonyl and the second acting in antagonism. As has been mentioned the phenyl group is capable of readily taking up an impressed polarity and hence it seems to act according to the first mechanism (VIII) markedly strengthening the C = O double bond.

VII VIII IX

Summary

The Raman spectra of the phenyl esters of cinnamic and benozic acids have been studied and those of the methyl and ethyl esters of the above acids along with that of phenyl acetate have been reinvestigated. From the above data and those obtained by other workers relating to alkyl and phenyl esters and some other carbonyl compounds the C = O frequencies have been tabulated. It is noted that the phenyl group attached directly to the carbon of the C = O group as in esters of aromatic acids and in aromatic ketones, etc., markedly lowers the carbonyl frequency whereas the same group attached to the oxygen atom of the COO group definitely enhances the frequency. These facts are explained from considerations of electromeric polarisation and resonance.

REFERENCES

1.	Murti and Seshadri ..	*Proc. Ind. Acad. Sci.*, 1938, **8**, 519.
2.	Narasimha Murti and Seshadri	*Curr. Sci.*, 1939, **8**, 209.
3.	Kohlrausch and Pongratz	*Wien. Ber.*, **142**, 637 ; *Mhchem.*, 1933, **63**, 12
4.	———— ..	*Wien. Ber*, **143**, 288 ; *Mhchem.*, 1934, **64**, 375.
5.	Matsuno and Han ..	*Bull. Chem. Soc.*, Japan, 1933, **8**, 333.
6.	Daure ..	*Ann. Physique*, 1929, **12**, 375 ;
	Kohlrausch, Koppel and Pongratz	*Z. Phys. Chem.*, Abt. B, 1933, **22**, 359 ;
	Simons ..	*Comm. Fenn.*, 1932, **6**, 13 ;
	Parthasarathy ..	*Phil. Mag.*, 1934, **17**, 471
	Paranjpe and Savanur ..	*Ind. J. of Phys.*, 1933, **8**, 503 ;
	Gorbeau ..	*Z. Phys. Chem.*, Abt. B, 1937, **38**, 45.

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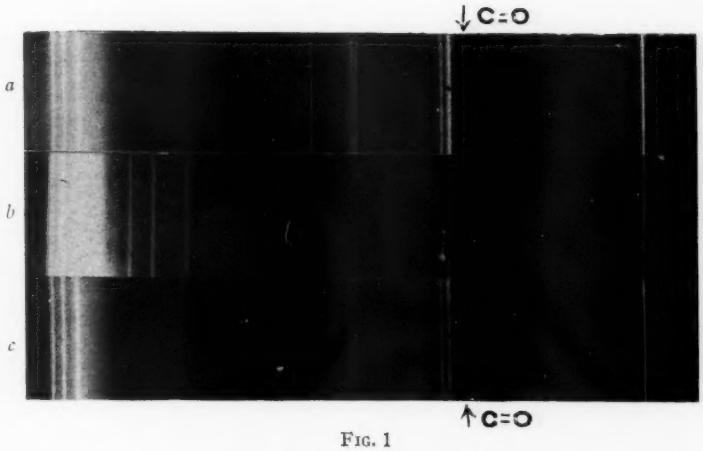

FIG. 1

(*a*) Ethyl cinnamate. (*b*) Phenyl cinnamate in carbon tetrachloride. (*c*) Methyl cinnamate.

FIG. 2

Phenyl acetate